

REMARKS

Reconsideration of the above-identified application in view of the foregoing amendments and following remarks is respectfully requested.

A. Status of the Claims and Explanation of Amendments

Claims 1-15, 17, 18 and 20-26 were pending. By this paper, claims 1, 5, 10 and 20 are amended, and claims 2, 4, 7, 11 are cancelled without prejudice or disclaimer.

Claims 1, 10 and 20 are amended to omit from the materials distributed in the polymer of the polymeric sheet “inorganic particulate.”

Formerly dependent claim 5 is amended into independent form. This amendment is not intended to narrow or otherwise alter the scope of claim 5 and is not made for any substantial reason related to patentability (§§ 102, 103). No new matter will be added by entry of this amendment.

Entry of these amendments is request as canceling rejected claims, simplifying the matters for appeal, and otherwise placing the claims in better condition for appeal.

Claims 1-4, 6-15, 17, 18, 20-26 were rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by U.S. Patent No. 6,130,175 to Rusch et al. (“Rusch”). [10/6/06 Office Action at pp. 2-3]. Claim 5 also was rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Rusch in view of U.S. Patent No. 5,147,722 to Koslow (“Koslow”). [10/6/06 Office Action at p. 3].

B. The Office Action Is Incomplete And Must Be Withdrawn;
Finality is Premature

The pending office action purports to reject each of the pending claims.

However, the office action does not address each and every claim, and is otherwise incomplete. Accordingly, finality is premature. See MPEP §706.07 (“Before final rejection is in order a clear issue should be developed between the examiner and applicant.”)

Specifically, a review of the office action finds that numerous features of the pending claims are not addressed in the office action. Some examples are as follows:

<u>Claim</u>	<u>Exemplary Claim Language Not Addressed</u>
9	“the polymeric sheet has distributed therein platinum supported on a substrate”
13	“wherein the polymeric sheet has an organic polymer distributed therein”
15	“wherein the membrane is disposed between two fuel cell electrodes”
17	“wherein the polymeric sheet has a thickness of less than 38 microns, and wherein the membrane that is disposed between said two electrodes of a fuel cell provides a steady state current of at least 1.78 amps/cm ² at 0.5 volts, with no humidification of incoming fuel cell air and hydrogen reactants, with air and hydrogen feed both at 40 psig and 25°C, and the fuel cell temperature at 50°C”
18	“c) said porous structure being substantially filled with a polymeric gel that contains electrolyte to provide ionic conductance for use in the electrochemical apparatus or process”
24	“wherein said ion-exchange resin is fluorinated”

Accordingly, the rejection of these claims is deficient, and should be withdrawn. To the extent that the rejection is maintained, Applicants request that the detailed factual basis therefore be stated in a non-final rejection. See In re Oetiker, 24 U.S.P.Q. 2d 1443, 1447 (Fed. Cir. 1992) (Plager, J., concurring) (“The examiner cannot

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sit mum, leaving the applicant to shoot arrows into the dark hoping to somehow hit a secret objection harbored by the examiner.”)

C. Rusch Does Not Qualify As Section 102(b) Prior Art

The office action asserted that Rusch is prior art to the present application pursuant to 35 U.S.C. § 102(b). [10/6/06 Office Action at p. 2]. However, Rusch is a U.S. patent that issued on October 10, 2000. This is more than three years after the earliest effective filing date of the present application (i.e., September 12, 1997 or the filing date of the grandparent application serial no. 08/928,207). Accordingly, Rusch is not Section 102(b) prior art to the present application.

D. Claims 1, 3, 6, 8-10, 12-15, 17, 20 and 22-25
Are Patentably Distinct From Rusch

In any case, the rejections of claims 1, 3, 6, 8-10, 12-15, 17, 20, and 22-25 are respectfully traversed for the further reasons discussed below. In particular, Rusch fails to teach, disclose or suggest a polymeric sheet having distributed therein “i) inorganic particulate; ii) metal; iii) an organic polymer; or iv) a combination thereof” as recited in Applicants’ claim 1.

Specifically, Applicants’ claim 1 recites:

“1. An integral, substantially air impermeable polymeric membrane for use in an electrochemical apparatus or process comprising:

- a) a polymeric sheet comprising polymer and having a porous structure with a microstructure of fibrils,
- b) the polymeric sheet having distributed in the polymer:
 - i) inorganic particulate;

- ii) metal;
- iii) an organic polymer; or
- iv) a combination thereof, and
- c) said porous structure being at least partially filled with an ion-exchange resin to provide ionic conductance for use in the electrochemical apparatus or process.”

Rusch is directed to an integral multi-layered ion-exchange composite membrane. In one embodiment, a thin integral composite membrane is comprised of a microporous polymer film, an ion-exchange polymer resin provided on one side of that microporous polymer film and another, different ion-exchange polymer resin provided on the other side of that microporous polymer film. [3/17-25; Figures 1-3].

For example, Figure 1 depicts a composite membrane (10) having a microporous film (11) and ion-exchange resin materials (12, 13) embedded in the pores on either side of film (11) [5/11-15]:

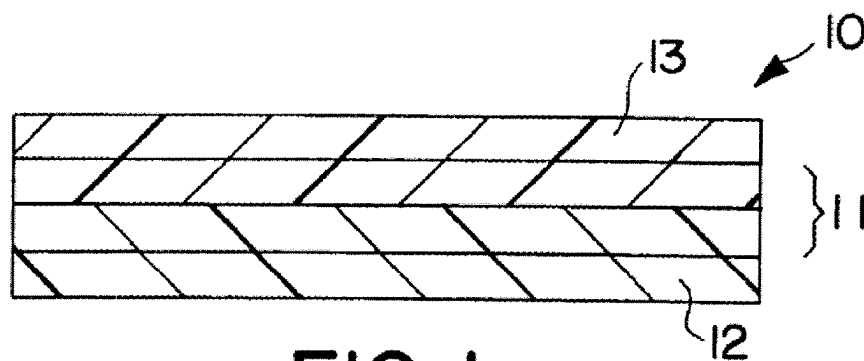


FIG. 1

The office action contends that Rusch's microporous film (11) corresponds to the “polymeric sheet” recited in Applicants' claim 1, and that Rusch discloses that this

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film (11) has inorganic particulate, metal, organic polymer or a combination distributed in the polymer itself. [10/6/06 Office Action at p. 2 (citing column 8, lines 41-56)].

Respectfully, this understanding of Rusch is inaccurate. The text spanning column 7, line 1 through column 8, line 56 relates to the ion exchange polymeric resin, and not the microporous polymeric film. The text cited by the office action discloses that certain materials may be incorporated into the ion exchange resins that are coated on the sides of film (11):

“Optionally, the *ion-exchange resin materials may be complemented by containing* finely divided powders or other non-ionic polymers to provide final composites. Such a finely divided powder may be selected from a wide range of organic and inorganic compounds such as, but not limited to, a metal oxide, carbon black, graphite, nickel, silica, titanium dioxide, platinum black, for example, to provide specific added effects such as different aesthetic appearance (color), electrical conductivity, thermal conductivity, catalytic effects, or enhanced or reduced reactant transport properties. Examples of non-ionic polymers include, but are not limited to, polyolefins, other fluoropolymers such as polyvinylidene fluoride (PVDF), or other thermoplastics and thermoset resins. Such non-ionic polymers may be added to aid occlusion of the substrate matrix, or to enhance or reduce reactant transport properties.” (emphasis added).

This passage clearly describes that it is the ion-exchange resin materials – not the microporous polymer film – that may be complemented with finely divided powders or non-ionic polymers. Claim 9 of Rusch similarly recites “the first, the second, or the first and second ion-exchange material contains a finely divided powder.” [18/4-6].

Further, we note that the passage at column 6, lines 27-37 describes formation of certain porous films by incorporating particular materials into the polymer. The first two patents, U.S. Patent Nos. 3,214,501 and 3,640,829 (attached as Exhibits A and B), describe that certain materials (starch, salt) are initially blended into a polymer and ***then are removed*** therefrom after forming the final article (e.g., a sheet).

The last patent, U.S. Patent No. 3,870,593 (attached as Exhibit C), describes the addition of finely divided particles of a non-hygroscopic inorganic salt to a polymer, forming a film, and then expanding the film to create porosity. [6/32-35; 9/22-10/6]. Such inorganic salts (e.g., calcium carbonate) would not constitute “i) metal; ii) an organic polymer; or iii) a combination thereof” as recited in Applicants’ claim 1. Independent claims 10 and 20, and dependent claims 3, 6, 8-9, 12-15, 17, and 22-25 are patentably distinct from Rusch for at least similar reasons.

E. Claim 5 Cannot Be Rejected Pursuant to Section 103 As Being Unpatentable Over Rusch Alone Or In Combination with Other References

The rejection of claim 5 is respectfully traversed. This claim was alleged in the office action as being unpatentable over Rusch in view of Koslow. As set forth below, Rusch may not be applied in such a Section 103 reference against the present application.

At best, Rusch might qualify as a cited reference pursuant to Section 102(e). *See supra* (beginning at 9). Applicants note that this reference is assigned to Gore Enterprise Holdings, Inc. (“Gore”), the assignee of the present application. Gore’s

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ownership of the present application and Rusch may be seen in the assignment records of the U.S. Patent & Trademark Office:

<u>Application</u>	<u>Reel</u>	<u>Frame</u>	<u>Date of Recordation</u>
Present Application	013883	0860	August 18, 2003
Rusch	013380	0048	October 9, 2002

Thus, the present application and Rusch were, at the time the invention of the present application was made, owned by Gore.

Section 103(c)(1) of the Patent Statute forbids the use of such a reference in an obviousness rejection against a commonly owned patent application:

“Subject matter developed by another person, which qualifies as prior art only under one or more of subsections (e), (f), and (g) of section 102 of this title, shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the claimed invention was made, owned by the same person or subject to an obligation of assignment to the same person. (35 U.S.C. §103(c)(1)).”

Accordingly, Applicants request withdrawal of the rejections based upon Section 103 on this further basis.

F. Claims 18, 21 and 26 Are Patentably Distinct From Rusch

The rejections of claims 18, 21 and 26 are traversed because the only cited reference, Rusch, fails to teach, disclose or suggest “said porous structure being

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substantially filled with a polymeric gel that contains electrolyte to provide ionic conductance” as recited in Applicants’ claim 18.

As noted *supra* at 9, the pending office action does not address this claim element. Applicants’ review of Rusch finds no such disclosure. The words “polymeric gel” are not used by Rusch. Accordingly, at least applicants’ claim 18 is patentably distinct from Rusch. Claims 21 and 26, both dependent from claim 18, are patentably distinct from Rusch for at least similar reasons.

Applicant has chosen in the interest of expediting prosecution of this patent application to distinguish the cited documents from the pending claims as set forth above. These statements should not be regarded in any way as admissions that the cited documents are, in fact, prior art. Likewise, Applicant has chosen not to swear behind Rusch, cited by the office action, or to otherwise submit evidence to traverse the rejection at this time. Applicant, however, reserves the right, as provided by 37 C.F.R. §§ 1.131 and 1.132, to do so in the future as appropriate. Finally, Applicant has not specifically addressed the rejections of the dependent claims. Applicant respectfully submits that the independent claims, from which they depend, are in condition for allowance as set forth above. Accordingly, the dependent claims also are in condition for allowance. Applicant, however, reserves the right to address such rejections of the dependent claims in the future as appropriate.

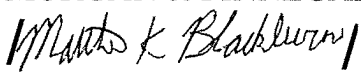
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CONCLUSION

For the above-stated reasons, this application is respectfully asserted to be in condition for allowance. An early and favorable examination on the merits is requested. In the event that a telephone conference would facilitate the examination of this application in any way, the examiner is invited to contact the undersigned at the number provided.

THE COMMISSIONER IS HEREBY AUTHORIZED TO CHARGE ANY ADDITIONAL FEES WHICH MAY BE REQUIRED FOR THE TIMELY CONSIDERATION OF THIS AMENDMENT UNDER 37 C.F.R. §§ 1.16 AND 1.17, OR CREDIT ANY OVERPAYMENT TO DEPOSIT ACCOUNT NO. 13-4500, ORDER NO. 0769-4624US5.

Dated: November 7, 2006

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EXHIBIT A

Oct. 26, 1965

H. J. STRAUSS

3,214,501

METHOD OF MAKING NON-ADHESIVE, HIGHLY COHESIVE MICROPOROUS
PLASTIC BANDAGE MATERIAL OR THE LIKE

Filed Sept. 12, 1961

2 Sheets-Sheet 1

Fig. 1

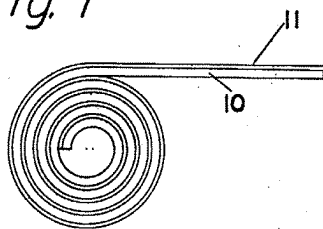


Fig. 2

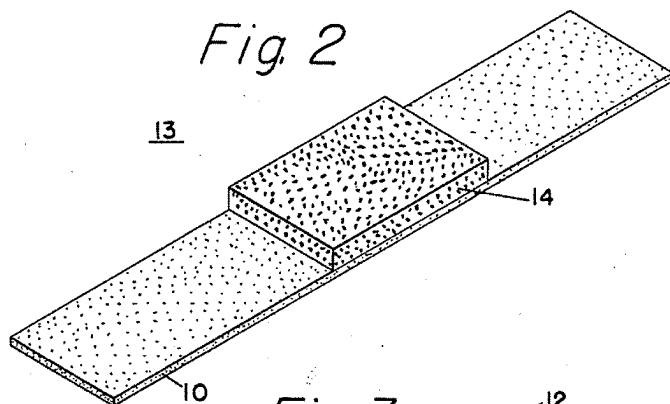
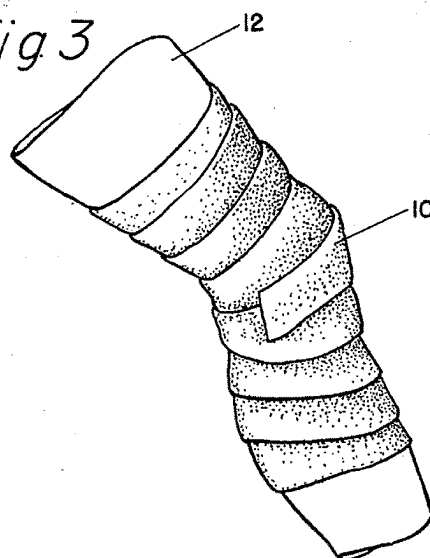


Fig. 3



Oct. 26, 1965

H. J. STRAUSS

3,214,501

METHOD OF MAKING NON-ADHESIVE, HIGHLY COHESIVE MICROPOROUS
PLASTIC BANDAGE MATERIAL OR THE LIKE

Filed Sept. 12, 1961

2 Sheets-Sheet 2

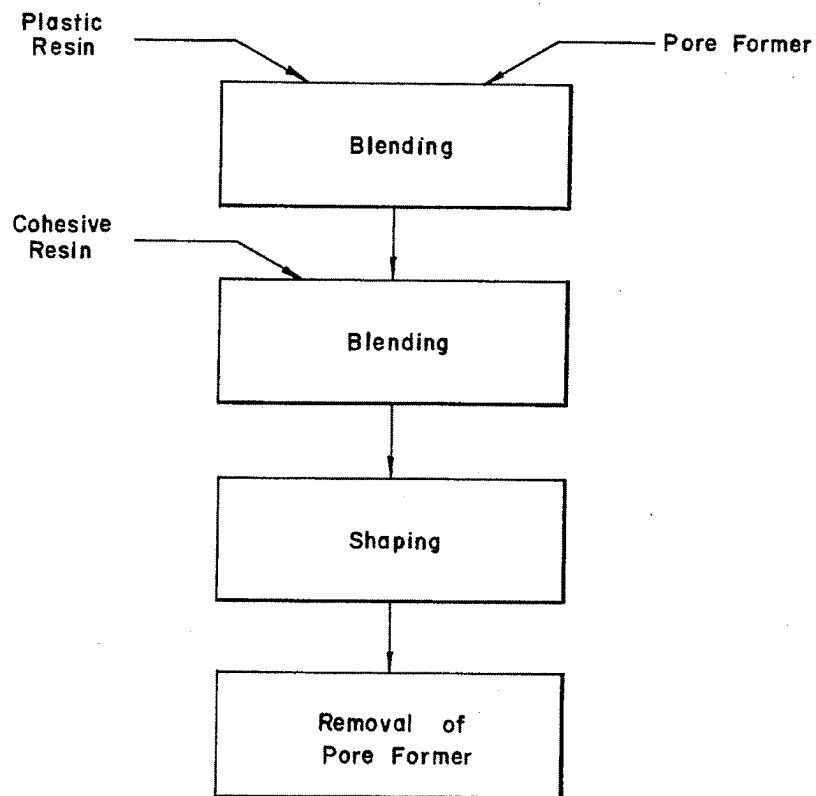


Fig. 4

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3,214,501

METHOD OF MAKING NON-ADHESIVE, HIGHLY COHESIVE MICROPOROUS PLASTIC BANDAGE MATERIAL OR THE LIKE

Howard J. Strauss, Elkins Park, Pa., assignor to Esb-Reeves Corporation, Glenside, Pa., a corporation of Delaware

Filed Sept. 12, 1961, Ser. No. 137,658

11 Claims. (Cl. 264-49)

This invention relates to the method of making a non-adhesive, highly cohesive microporous plastic sheet material and has for an object the provision of a non-adhesive, highly cohesive microporous plastic particularly suitable for bandages or the like and method of making the same.

In the preparation of microporous plastic materials which are to be laminated to other sub-strata, one of the principal difficulties encountered is in providing a proper adhesive to the sub-strata layer which will not interfere with the ability of the microporous material to "breathe." Such adhesive-coated microporous plastic materials are particularly suited for use as adhesive bandages and other surgical wrappings and dressings. The difficulty encountered heretofore is that the application of an adhesive to the microporous plastic materials reduces the total vapor or gas transmission of such a microporous plastic by an amount controlled by the surface area of the microporous plastic covered by the adhesive and the vapor or gas transmission characteristics of the adhesive itself. Adhesives commonly used for such purpose have substantially no gas or vapor transmission and the application of such adhesives in a geometrical pattern, even though in very fine lines of adhesive, cuts down the overall transmission available by that fraction of the surface which is covered by the adhesive itself. This has been the normal approach in the past to the application of adhesives to bandage backings. An alternative approach used heretofore has been the application of extremely thin layers of adhesives which do provide a small amount of vapor or gas transmission. Such adhesives are usually applied over the entire surface, and while the adhesive does cut down the gas and vapor transmission by an amount governed by its resistance to the diffusion of such materials, as long as a sufficient layer of adhesive can be maintained, the effectiveness of the microporous material will not be completely removed.

The present invention eliminates the need of providing the microporous plastic material with an adhesive on the surface thereof. It makes an ideal material for use as bandages, surgical wrappings or dressings since it is non-adhesive and, thus, does not adhere to the body. The microporous plastic of the present invention by being highly cohesive sticks tightly to itself but does not decrease its microporosity to a substantial degree.

In accordance with the present invention, a highly cohesive resin is physically alloyed with a plastic base prior to its being made microporous. In this way, a high degree of cohesiveness can be imparted to the microporous resin itself, and by the selection of a proper cohesive material, as for example butyl rubber, this property can be achieved without any significant degree of adhesiveness being imparted to the finished product.

Further in accordance with the invention, there is provided a method of making a non-adhesive, highly cohesive plastic sheet material by alloying a highly cohesive resin with a plastic base at a temperature within the softening range of the resin and plastic, forming the alloy into a sheet, and thereafter making the sheet microporous to increase its cohesive power.

More particularly, the present invention provides a

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method of making a non-adhesive, highly cohesive plastic sheet material by blending together polyethylene and finely divided starch at an elevated temperature and for a time sufficient to soften the polyethylene and below that which produces charring of the starch, blending the mixed polyethylene and starch with butyl rubber, and thereafter shaping the alloy of polyethylene, starch and butyl rubber into sheet material, and leaching the starch particles from the alloy to produce microporosity of the sheet material with a resultant increase in its cohesive power.

For further objects and advantages of the invention, reference is to be had to the following description taken in conjunction with the accompanying drawings in which:

FIG. 1 is an elevational view of a roll of non-adhesive, highly cohesive microporous plastic strip material embodying the present invention;

FIG. 2 is a perspective view of a strip-type bandage and pad of the microporous material embodying the present invention; and

FIG. 3 is a perspective view illustrating the cohesive microporous material used as a finished bandage; and

FIG. 4 is a flow diagram illustrating the method of making a non-adhesive, highly cohesive microporous plastic material in accordance with this invention.

Referring to FIG. 1, the non-adhesive, highly cohesive microporous plastic material has been shown as a strip 10 having a release paper or fabric strip 11 on one side to prevent sticking of the microporous material 10 when it is supplied in roll form. The microporous material 10 may be produced by blending together polyethylene and finely divided starch at an elevated temperature and for a time sufficient to soften the polyethylene and below that which produces charring of the starch. A suitable mixture has been found to be about 100 parts of polyethylene to 400 parts of corn starch. The polyethylene and starch may be blended within the temperature range of about 220° F. to 320° F. Charring of the starch is minimized at the higher temperatures by mixing it rapidly and for a shorter period of time than at the lower temperatures. A suitable method of mixing the starch and polyethylene is described and claimed in U.S. Patent 2,676,929, Duddy, where continued wiping action takes place by differential rolls.

When the starch and polyethylene are thoroughly blended, butyl rubber in the order of 50 parts is milled into the mixture before transferring the mixture to a calender where it can be sheeted to the desired form. The mixing or blending of the butyl rubber is done in the same temperature range as mentioned above. It is also to be noted that because of the plasticization action of the butyl rubber, the mixture can also be readily extruded. The order of mixing is not particularly critical. However, the above sequence of steps has been found to be satisfactory.

After shaping of the mixture of starch, polyethylene and butyl rubber into sheet material, the sheet material is immersed in an aqueous bath at a temperature below that which produces substantial expansion of the starch particles. This may be accomplished by immersing the sheet material in plain water, or alternatively, in an alkaline solution about 2% sodium hydroxide at a temperature not exceeding about 140° F. The temperature of the bath is then raised to about its boiling point for expansion of the starch particles. The expanded starch particles are then removed from the sheet material to produce microporosity of the sheet material. The starch removal may be accomplished by leaching. The sheet material may be immersed in a dilute solution of acid, such as sulphuric acid, of 2% to 3% maintained at 210° F. which hydrolyzes and solubilizes the starch. The time

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required for removal of the starch is relatively short since the sheet material is relatively thin, such time being in the order of about ten to fifteen minutes.

The pore size of the microporous material may be controlled by selection of the starch used as the pore forming agent. Where fine pores are required, for example as in the case of the microporous plastic adhesive bandage backing material 10, FIGS. 1-3, the pore forming agent may be selected from the starches which have fine particle sizes such as rice, corn or wheat. Where a significantly larger pore size is desired, as in the pad 14 of the bandage, FIG. 2, a coarser particle size starch, such as potato starch would be used. In addition, the method of starch removal involves first swelling the starch in boiling water. Subsequently, the starch is removed by solubilizing through hydrolysis. If the hydrolyzing bath is above the deformation temperature of the plastic, the pores so formed will be free to return to their original size, i.e., the size of the particle of starch from which they were formed. This is referred to as the normal pore form. If however the hydrolysis is carried out at temperatures sufficiently low to prevent thermal movement of the plastic, the pore will assume the size of the expanded particle of starch, i.e. referred to as the expanded pore form. Thus it is possible to control the size of the pore from very small sizes (i.e., of the order of 1 micron) all the way up to extremely coarse pores (i.e., of the order of 300 microns) by a combination of the selection of the particular source of starch and the preparation to expanded or normal pore form.

The resultant sheet produced by the above method is highly microporous with a good interconnecting pore structure which provides for high vapor and gas transmission. The butyl rubber does influence the properties of the resultant sheet to the extent that it increases the elasticity and elongation over that of pure polyethylene, but to some degree reduces the tensile strength. This combination of properties is quite satisfactory for bandage applications, and as a matter of fact the increased elasticity permits application of the bandage to highly irregular surfaces.

Such an application of the microporous sheet material 10 is shown in FIG. 3 where the material has been used as the bandage for a knee of leg 12. Such types of bandages or wrappings are particularly useful to athletes in wrapping various joints of the body. The sheet material 10, by reason of its microporosity and inclusion of butyl rubber, is highly cohesive and, thus, readily sticks to itself when one layer engages another. This prevents the various layers of the bandage 10 from slipping relative to each other. At the same time the material 10 of the bandage, by being microporous, permits the leg 12 to breathe through the bandage. The overlapping of the layers of the bandage 10 does not sacrifice to any substantial degree the original porosity and/or gas and vapor transmission of the material 10. The material 10, by reason of its increased elasticity, permits the knee to be bent when wrapped in a bandage as shown in FIG. 3. This minimizes discomfort to the wearer. It has also been found that the gas and vapor transmission and cohesion both are improved by a slight stretching of the material 10 during its application.

Since the material 10 is highly cohesive, it sticks to itself and no additional adhesive is required to maintain the bandage in place. Additionally, since the material 10 is non-adhesive, it does not adhere to the skin of the wearer.

In FIG. 2 there is shown a bandage 13 including a strip of the material 10 having cohesively attached thereto a pad 14 of the non-adhesive, highly cohesive microporous plastic material. The microporous material 14 is provided with larger pores, as above described, than those in the strip 10. This permits the pad 14 which is adapted to engage the wound or cut to absorb the blood or other fluid and at the same time permits gas and vapor trans-

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mission through not only the pad 14 but also the bandage 10. The pad 14 is cohesive with the bandage strip 10 and, thus, it will remain in place relative to the strip 10 in the manner shown in FIG. 2. However, since the pad 14 is non-adhesive, it does not stick to the wound and, thus, minimizes discomfort to the patient when the bandage or dressing is being changed or removed. All that is necessary to maintain the bandage 13 in place is to wrap the end portions of the strip 10 so that they will overlap each other. The overlapping portions are maintained in engagement by the cohesive power of the microporous material.

By mixing the starch, polyethylene and butyl rubber in the ratio of about 4:1:½ and thereafter removing the expanded starch particles, there results a plastic alloy which is microporous. The rubber is chemically unchanged and imparts to the alloy its characteristics. It has been found that when the ratio of starch to plastic material (i.e., polyethylene plus alloying resin) falls below the ratio of 2:1, there is a very sharp and significant fall-off in the water vapor transmission capabilities of the resultant sheet material. The theory as to why the microporous alloy of polyethylene and butyl rubber has such high cohesive power is not fully understood, but it is believed to be due to the fact that the surface of the material, although apparently smooth, is microscopically very rough and very extended due to the microporosity and, thus, enables rubber-to-rubber contact over a greater area than would be possible for a non-microporous alloy of polyethylene and butyl rubber. It has been found that the cohesive power of the microporous alloy of polyethylene and butyl rubber produced in accordance with the present invention is several times greater than that of non-microporous polyethylene and butyl rubber.

Removable solid fillers of the anhydrous type other than starch may be used, such, for example, as dry powdered sugar or salt. The starch may be replaced in whole or in part by the sugar and in approximately the same proportions since sugar and starch have approximately the same specific gravities. Where salt is used as the filler, it is necessary to replace the starch by approximately twice its weight of salt to compensate for the differences in specific volumes.

While the preferred form of the invention has been described and illustrated, it is to be understood that other modifications thereof may be made within the scope of the appended claims.

What is claimed is:

1. The method of making a non-adhesive, highly cohesive microporous plastic sheet material which comprises mixing and blending together polyethylene and finely divided starch in ratio of starch to polyethylene of about 4:1, during the blending applying at elevated temperature a continued wiping action by differential rolls, said temperature being within the range of a softening temperature of polyethylene and below that which produces charring of the starch, blending butyl rubber into the mixture of polyethylene and starch to form a composition having a ratio of starch to polyethylene to butyl rubber of about 4:1:½, shaping the mixture of starch, polyethylene and butyl rubber into sheet material, immersing the sheet material in an aqueous bath at a temperature below that which produces substantial expansion of the starch particles, thereafter elevating the temperature of the bath for expansion of the starch particles, and leaching the expanded starch particles from the mixture to produce microporosity of the sheet material.

2. A method for making a non-adhesive, highly cohesive microporous plastic comprising the following steps: (a) blending a composition consisting essentially of a highly cohesive resin, a plastic resin base material and a pore forming agent at a temperature within the softening range of said cohesive resin and plastic resin base material, with said plastic resin base

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- material being present in a major amount and said cohesive resin being present in a minor amount,
- (b) forming the blended resins into a predetermined shape, and
- (c) removing said pore forming agent from the shaped resin blend to render it microporous.
3. A method in accordance with the method of claim 2 in which the pore forming agent is selected from the group consisting of starch, sugar and an inorganic salt.
4. A method in accordance with the method of claim 3 in which the plastic resin base material is polyethylene.
5. A method in accordance with the method of claim 4 in which the cohesive resin is butyl rubber.
6. A method in accordance with the method of claim 5 in which the pore forming agent is starch, and the ratio of starch to polyethylene plus butyl rubber is at least about 2:1.
7. A method of making a non-adhesive, highly cohesive microporous plastic comprising the steps of:
- (a) blending a composition consisting essentially of a plastic resin base material and a pore forming agent at a temperature within the softening range of said plastic resin base material,
- (b) incorporating a minor amount of a highly cohesive resin into the composition of step (a) and thoroughly blending the resulting mixture at a temperature within the softening range of said cohesive resin and plastic resin base material,
- (c) forming the resin blend into a predetermined shape, and
- (d) removing said pore forming agent from the shaped resin blend to render it microporous.

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8. A method in accordance with the method of claim 7 in which said pore forming agent is selected from the group consisting of starch, sugar and an inorganic salt.
9. A method in accordance with the method of claim 8 in which the plastic resin base material is polyethylene.
10. A method in accordance with the method of claim 9 in which the cohesive resin is butyl rubber.
11. A method in accordance with the method of claim 10 in which the pore forming agent is starch, and the ratio of starch to polyethylene plus butyl rubber is at least about 2:1.

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ROBERT F. WHITE, *Primary Examiner*.30 RICHARD J. HOFFMAN, MORRIS LIEBMAN, ALEXANDER H. BRODMERKEL, *Examiners*.

EXHIBIT B

United States Patent

Elton

[15] 3,640,829

[45] Feb. 8, 1972

[54] MICROPOROUS PRODUCTS

- [72] Inventor: Robert L. Elton, White Bear Lake, Minn.
 [73] Assignee: Minnesota Mining and Manufacturing Company, St. Paul, Minn.
 [22] Filed Oct. 20, 1969
 [21] Appl. No.: 867,538

- [52] U.S. Cl. 161/159, 156/77, 161/164,
 161/191, 260/2.5, 264/344
 [51] Int. Cl. B32b 3/26, C08g 22/44, D06n 3/14
 [58] Field of Search 260/2.5 AC, 2.5 AL, 2.5 AN, 2.5 A,
 260/2.5 AY; 156/77-79, 209, 219, 220; 117/62.1,
 63, 135.5; 161/151, 159, 160, 164, 191; 264/48, 49,
 45, 344

[56] References Cited

UNITED STATES PATENTS

- 3,244,673 4/1966 Bruin et al. 260/2.5 X

3,418,198 12/1968 Einstman 161/84

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[57]

ABSTRACT

In the disclosed method of making a microporous sheet material a heat-formed (extruded, calendered, or pressed) film comprising (1) a polyurethane (preferably combined with an epoxidized soybean oil processing aid—a water insoluble plasticizer can also be included) capable of forming a non-porous film having a storage shear modulus (G') of about 0.4 to 5×10^8 dynes/cm.² and a loss tangent at 0.2 cycle/sec. less than 0.5, both measured at 23° C., and (2) distributed throughout the film, a plurality of <30 micron salt (e.g. NaCl) particles, is annealed prior to leaching of the salt from the film with an aqueous medium. The resulting microporous film is useful in making leatherlike sheet materials. Preferably, the film is embossed prior to leaching but after annealing.

9 Claims, 2 Drawing Figures

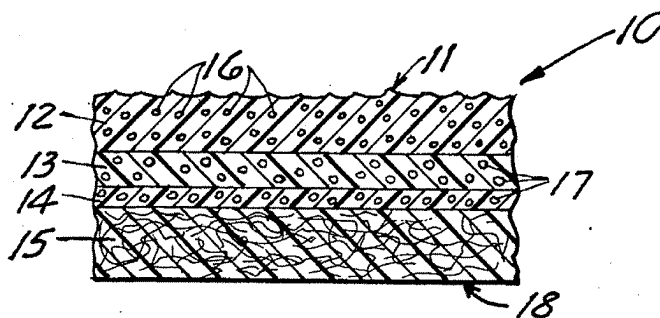


FIG. 1

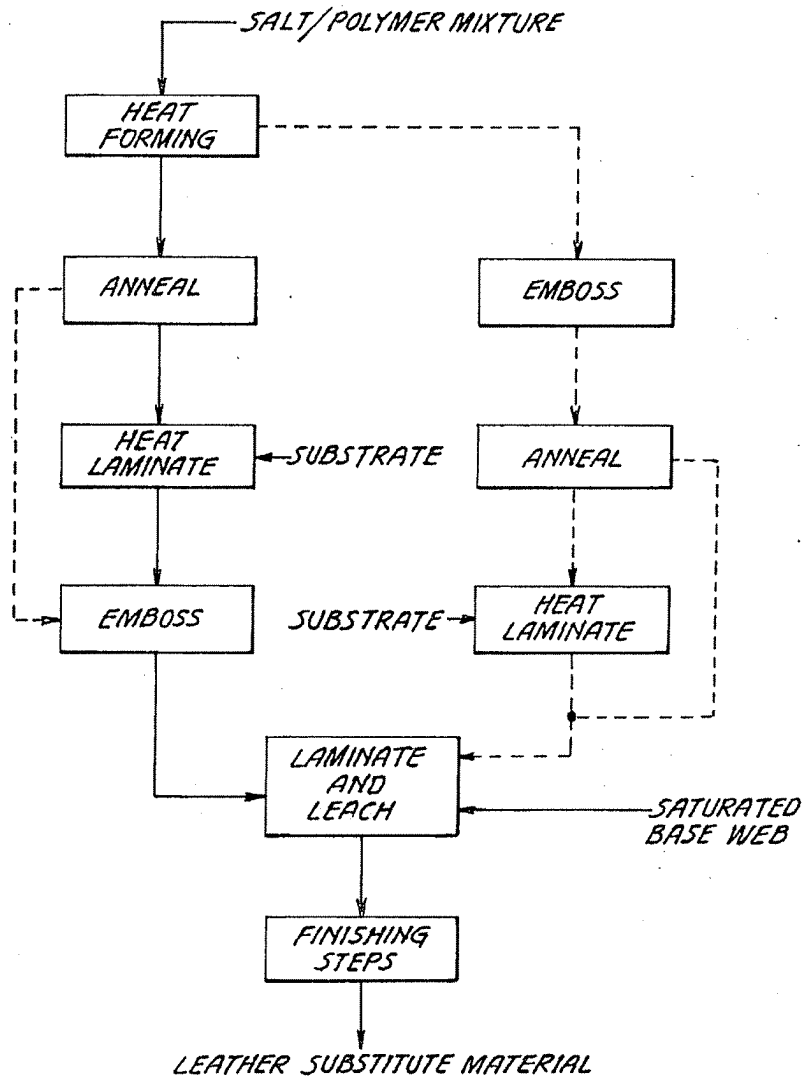
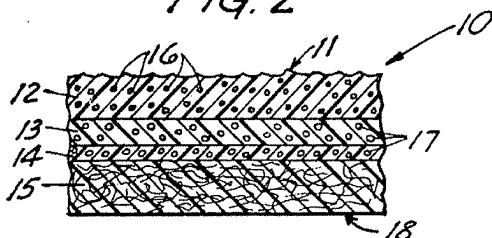


FIG. 2



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MICROPOROUS PRODUCTS

FIELD OF THE INVENTION

This invention relates to leatherlike microporous films and methods for making them. An aspect of this invention is that the disclosed leatherlike films are suitable for use in quality men's shoe upper material. A further aspect of this invention is that the salt-leach technique of introducing microporosity into a polymeric film is adapted for use with heat-formed (extruded, calendered, or pressed) polyurethane films.

DESCRIPTION OF THE PRIOR ART

Several methods are well known for their ability to produce leatherlike films from polyvinyl chloride, polyurethanes, and other synthetic organic polymers. Since a nonporous film of synthetic polymer does not transmit moisture effectively, it is essential—particularly when making a leather substitute to be used in high-quality men's shoes—to introduce porosity (especially microporosity) in some manner. Unfortunately, increasing the moisture vapor transmission (M.V.T.) of a synthetic polymeric film by increasing its porosity often degrades its other physical properties, e.g., scuff or abrasion resistance, tensile strength, physical appearance or feel. The term "microporous" is generally understood to refer to pores which are invisible to the naked eye, i.e., less than about 30 microns in their widest dimension. Pores 30–100 microns in diameter or width are very difficult to see, but are not generally considered microscopic, because they often affect the appearance of the surface of the film even if individual pores cannot be clearly distinguished.

Methods commonly used to provide microporosity are:

1. The solvent/nonsolvent technique: In this method a polyurethane "solution" (which may, in fact, be a highly solvated dispersion) is at least partially gelled with a nonsolvent for the polymer; a film containing entrapped solvent is cast from the gelled solution; and the entrapped solvent is washed out of the film with nonsolvent. This method is suitable for use with linear polyurethanes only. See, for example, Holden, U.S. Pat. No. 3,100,721, issued Aug. 13, 1963.

2. The water-laid sheet technique: In this method a polymer dispersion or latex is waterlaid in accordance with papermaking technology. The resulting sheet is carefully pressed and/or heated to an integral, porous film; see, for example, Raymond et al., U.S. Pat. No. 3,436,303, issued Apr. 1, 1969.

3. The high-boiling organic liquid droplet technique: In this method a polymeric latex containing suspended droplets of a high-boiling organic liquid such as mineral spirits is cast to form a film, dried (i.e., water is removed), and heated to drive off the organic liquid. See Newton, U.S. Pat. No. 3,445,272, issued May 20, 1969.

4. The foaming technique: In this method the polymeric film is made porous by means of a discontinuous gas phase which escapes from the surface of the film, in some processes before the film has been fully cured or hardened. See, for example, British Pat. specification No. 727,321, published Mar. 30, 1955.

5. The crushable filler technique: In this method the film is formed with a filler in it which is crushable. The film is passed through pressure rolls and the fracturing of the filler particles leaves voids in the material; see Dosmann, U.S. Pat. No. 3,143,436, issued Aug. 4, 1964.

6. The leachable solid filler technique: In this method an integral polymeric layer (an uncured liquid, a coating of polymeric solution, or a heat-formed film) containing a water-soluble filler such as finely divided sodium chloride is leached out with water. The water removes the filler, leaving voids in the layer; see, for example, the aforementioned British Pat. No. 727,321, British Pat. Nos. 727,679, 844,801, and 1,132,594, U.S. Pat. Nos. 2,819,981, 2,835,607, 3,387,989, etc.

Most of the above techniques either sacrifice the other previously mentioned physical properties or present quality control problems—the size, amount, shape, and distribution of

the pores cannot be precisely controlled without a great deal of sophisticated know-how, and, in some cases, cannot be adequately controlled at all. Other problems include "mud cracking," curling, and uncontrolled variations in the caliper of the film. For example, in the solvent/nonsolvent technique described in the Holden patent, the polymeric "solution" must be brought, by means of the addition of nonsolvent, to the point where it has become a true colloidal dispersion prior to the casting and washing steps. The addition of nonsolvent must be within very narrow limits, or else premature gelation can occur. Furthermore, even when the film is correctly cast and coagulated, it cannot take heavy embossing without loss of M.V.T.

The leachable solid filler technique, on the other hand, can be relatively easy to control, particularly when the polymeric layer is an integral solid sheet material which has been heat formed (extruded, pressed, or calendered) from a polymeric composition including the filler, and the filler thereafter leached out. These steps permit size, shape, and distribution of the pores in the heat-formed sheet to be controlled in a simple manner. The caliper (gauge or thickness) of the heat-formed sheet is under direct, positive control, and the properties of the polymer used in the film can be determined in advance by the simple expedient of selecting an already-formed polymer, no curing or in situ polymerization steps being involved.

Good M.V.T. values have been obtained when a coating is cast from a polyurethane solution containing sodium chloride and the sodium chloride is leached from the coating; but, uneven caliper, curling, and mud-cracking problems can result during processing of the cast film, particularly when it is cast to a dry thickness of about 5 mils (125 microns) or more.

A better way to achieve good M.V.T. values is set out in British Pat. Nos. 727,679 and 844,801, which disclose (1) mixing dry, particulate polyvinyl chloride (hereinafter P.V.C.) or natural rubber with NaCl powder, plasticizer, and solvent, (2) extruding the mixture to form a film, (3) removing the solvent, and (4) leaching the salt-filled film with water. Caliper can be controlled, and there is freedom from both curling and mud cracking. Thus, the aforementioned British technique appears to be an attractive prospect for adaption to other polymers besides P.V.C. and natural rubber, e.g., for polyurethanes. Experience shows, however, that there is no straightforward way of substituting a polyurethane starting material in the processes of British Patent Nos. 727,679 and 844,801. Polyurethane films are not commonly formed by extrusion, and it is difficult to predict the effect of processing steps, solvents, plasticizers, other processing aids, etc., upon such properties as flex life and scuff resistance in the final product. Unlike the typical vinyl polymers, the polyurethanes employed in making leather substitutes usually possess considerable inherent plasticity and elasticity. One could thus not predict that there would be any advantage to incorporating processing aids and plasticizers. Although the use of solvents in P.V.C. systems is optional, eliminating solvent from a heat-processed polyurethane system might be expected to necessitate fairly severe processing conditions. Furthermore, with or without processing aids or solvents, it might be supposed that the heat-forming step itself would have to be carried out uncomfortably close to the degradation temperature of the polyurethane, further complicating the predictability of results.

To sum up, it appears that the present state of the art shows a total lack of guidelines for adapting the leachable solid filler technique to a process utilizing a heat-formed (extruded, calendered, or pressed) inorganic salt-loaded polyurethane film, at least in terms of providing adequate M.V.T., scuff resistance, etc. Adequate M.V.T. can be obtained by casting a salt-loaded film from a polyurethane solution, but the advantages of positive control over caliper, elimination of mud cracking and curling and the like are then lost, particularly when films of at least 5-mil dried thickness are desired. The M.V.T. can, in any leachable filler method, be increased by increasing the filler loadings, but the scuff resistance and the

flex-fatigue resistance of the resulting microporous film is thereby reduced. Any worthwhile leachable filler method must provide high M.V.T. without unduly high filler loadings.

Good M.V.T., scuff resistance, etc., is not always required of a leather substitute, but in the quality (medium-to-high priced) men's shoe market, the standards of consumer acceptability are very exacting. Indeed, no leather substitute, regardless of how it is made, has fully and consistently met all the exacting criteria of this market, and customer acceptance of Oxford-type shoes made from the available leather substitutes has generally lagged behind the expectations and hopes of the synthetic leather and shoe industries. This fact is readily grasped when M.V.T. alone is considered: given a relative humidity difference of 50 to 100 percent on opposite surfaces of the material and a temperature of 73° F. (23° C.), the better grades of natural leather have M.V.T. values ranging from 2,500 to 4,000 g./hr./100 m.², but most commercially available imitation leather materials with even moderately good leatherlike properties have an M.V.T. below 2,000 gm./hr./100 m.².

Accordingly, this invention seeks to provide a leatherlike sheet material with high M.V.T., good scuff resistance, good flex-fatigue resistance, high tensile strength, leatherlike appearance and tactile qualities, and controlled thickness, without the problems of solvent handling.

This invention also contemplates a method of making a leatherlike microporous sheet which will not develop mud cracking or curling during processing.

This invention further contemplates adapting the solid filler leach technique for use with a polyurethane starting material such that none of the aforementioned properties or qualities are sacrificed and such that the leach time is not unduly lengthy.

This invention further contemplates providing a method of producing a heat-formed microporous polyurethane film wherein the size, amount, and distribution of the pores can be controlled simply and with great consistency.

This invention further contemplates a method for improving the M.V.T. of polyurethane films without sacrificing any other leatherlike quality.

It is still further contemplated that the polyurethane used in the process of this invention need not be linear, but may contain some cross-linking.

BRIEF DESCRIPTION OF THE INVENTION

It has been discovered that inorganic salt-filled polyurethane films which have been heat formed (extruded, calendered, or pressed) from a particulate mass can be leached with a solvent for the inorganic salt to obtain a microporous polyurethane film of any desired thickness, e.g., 5-30 mils, with good M.V.T. and other leatherlike properties, provided that: (all properties being measured at 23° C.)

First, the polyurethane starting material or materials (preferably blended with a processing aid) are capable of forming a film with a storage shear modulus (G') of about 0.4 to about 5×10^8 dynes/cm.² and a loss tangent (loss tan.) of less than 0.5 measured at a frequency of 0.2 cycle/sec. and 23° C.

Second, the heat-formed polyurethane film filled with the particulate, leachable filler is heat treated at a temperature which is high enough to relieve stresses in the film, but not so high as to cause degradation of the polyurethane. In short, at some time after the heat-formation of the filled polyurethane film, the film is annealed.

At a suitable time following the annealing step, the filler is leached from the film, and the resulting microporous structure has excellent M.V.T. Other steps can be included in the process of this invention; for example, an embossing step can either precede or follow the annealing step. It is preferable to emboss the film prior to leaching, so that either light or heavy embossing can be carried out without substantially affecting the M.V.T. value. Other optional steps include lamination of the heat-formed, annealed film to any suitable substrate and

various dyeing and finishing steps which further improve the appearance and/or leatherlike qualities of the film. Various mixing steps can be used to provide a filler/polyurethane composition prior to heat forming. The heat-forming and annealing steps, particularly if heat-forming is by pressing, can be carried out in a single equipment module. Regardless of the nature of the heat-forming step, however, it must be completed prior to the initiation of the annealing step.

The term "polyurethane," as used herein, denotes the materials commonly referred to by polymer chemists as "polyurethanes," including polyurethane-polyureas, polythiourethanes, and certain of the polyureas. This class of polymers has molecular chains containing at least one polyoxyalkylene and/or polyester component derived from active hydrogen-terminated compounds (such as polyester or polyoxyalkylene glycols), at least one component derived from an aromatic or an aliphatic poly(usually di- or tri-) isocyanate, and, optionally, a component derived from an active hydrogen-containing compound which extends, cross-links or terminates the polymer chain. A wide variety of available polyurethanes, both linear and cross-linked will satisfy the requirements of this invention; provided, that a particulate mass of the polyurethane can be heat formed into a film with the above mentioned storage shear modulus and loss tangent properties, particularly when a suitable processing aid is used to facilitate heat forming. In the case of cross-linked polyurethanes, the cross-link density should be very low to facilitate the heat-forming step, a typically suitable cross-link density being less than one cross-link per 50,000 polymer atomic weight units. It should also be borne in mind that, even in some so-called "linear" polyurethanes, there can be some cross-linking due to the formation of biuret or allophanate linkages. Linear polyurethanes having repeating units of the formula

$-O-Z^1-O-CO-NH-Ar-NH-CO-O-Z^2-O-CO-NH-Ar-NH-CO-$ are preferred, Z^1 being a polyoxyalkylene or polyester chain, and Z^2 being a polyoxyalkylene or polyester chain or an alkylene radical having two to six (preferably four) carbon atoms. Ar is a mono or polynuclear aromatic group. Suitable mononuclear aromatic groups are benzene, toluene, xylene, and other substituted phenyl groups, while suitable polynuclear aromatic groups may have either fused or separate rings, e.g., naphthalene, biphenyl, diphenyl methane, and the like.

The term "processing aid," as used herein, refers to a class of materials which can be used in polymeric systems to facilitate extrusion, calendering, or similar processing steps. Preferred processing aids are the epoxides of the unsaturated fatty acid glyceryl esters, described in detail hereinafter. A plasticizer such as a diester of a low molecular weight polyoxyalkylene glycol can optionally be included in the starting material along with the processing aid.

The invention can be readily visualized from the drawings, wherein:

FIG. 1 is a flow diagram of a preferred process for making microporous films and laminating them with a suitable base web, and

FIG. 2 is a cross-sectional view of a preferred form of leather substitute material made according to this invention.

DETAILED DESCRIPTION AND EXAMPLES

The discovery that annealing of a heat-formed, inorganic salt-filled polyurethane film permits the attainment of high M.V.T. upon leaching of the film to form a microporous structure is surprising, and has no simple theoretical explanation. It is well recognized that extrusion or calendering (and even pressing) of a particulate polymeric mass can introduce strains into the resulting polymeric film. It is also well known that heat tends to disorient the molecules of the film, thereby relieving patterns of strain. However, it is believed that it has not heretofore been recognized that relieving the strain in a salt-filled polyurethane film would increase the M.V.T. capabilities of the microporous film obtained by leaching out the filler.

Three possible reasons why this relationship between annealing and M.V.T. has not hitherto been perceived are: First, microscopic comparison of the annealed and unannealed films shows no obvious differences. Second, careful density comparisons reveal no measurable differences in void volume. Third, other means of eliminating strain (e.g., by reducing the stresses applied during the heat-forming step) do not provide the advantages of annealing.

Since annealing does not increase the void volume nor alter the microporous structure, at least in a manner which can be detected by microscopic or density studies, the explanation for the improved M.V.T. must be found elsewhere. Although this invention is not limited by any theory, it is theorized that the annealing step helps to preserve intercommunication or interconnection between the pores of the microporous film, even though such interconnection is not readily visible in microscopic studies. When two microporous films, identically processed except for the use of the annealing step of this invention with one of the films, are tested for porosity using the mercury porosimeter method (a test method wherein mercury is forced into the pores under pressure), some slight differences do appear. Even the porosimeter studies, however, do not suggest that a substantial increase in M.V.T. can be obtained by annealing. In actual practice, annealing according to this invention can double the M.V.T.; this surprisingly large increase in M.V.T. represents an improvement which can spell the difference between a leather substitute which will be at least potentially competitive with a good grade of natural leather and one which will not, particularly in the medium-to-high-priced men's shoe market.

In other words, the relief of strain patterns in the polymeric film is not the main reason for this annealing step. Strain patterns can be avoided by using plasticizers which permit low-stress extruding or calendering. The resulting strain-free films do not necessarily provide significantly improved M.V.T. after leaching, however.

Another advantage resulting from the annealing step is that the time required to leach the soluble filler is substantially reduced. In view of the negligible change in void volume and (apparently) pore structure attributable to annealing, this reduced leach time feature is equally difficult to explain. Perhaps the increased M.V.T. and reduced leach time are related phenomena. In any event, the economic burden of a long leach time has been reduced by my invention, thus bolstering the commercial feasibility of making heat-formed, microporous polyurethane films with the salt-leach technique.

There is also no simple explanation for the fact that my preferred processing aids improve or preserve the M.V.T. of the final product. Although this invention is not limited by any particular theory, this improvement may be related to the fact that the processing aid facilitates heat forming and/or to the possibility that it inhibits heat and/or oxidative degradation of the polyurethane film during processing.

It has been found that the presence of olefinic and epoxy (oxirane) functional groups in the molecules of the processing aid are desirable; hence, the aforementioned preference for processing aids comprising an epoxidized ester-type oil, i.e., an epoxidized glyceryl ester of a fatty acid which can contain unsaturation.

Epoxidized soybean oil has previously been used to plasticize P.V.C., and this epoxide is "compatible" with P.V.C. in virtually all proportions. ("Compatibility" is a term of art meaning ease of blending, and "compatible" plasticizers tend to be soluble in, form a single phase with, and/or exert a solvating effect upon at least a portion of the molecular structure of the polymer to be plasticized.) "Incompatibility" is generally considered undesirable in the P.V.C. art, since exudation of the plasticizer and tackiness of the polymer are considered undesirable.

In the present invention, however, the teachings of the plasticized P.V.C. art do not appear to be directly applicable. The partial incompatibility of the herein preferred processing aids appears to do no harm and may even contribute to their

facilitation of the processing and the improvement or preservation of M.V.T. At least one type of compatible material, the water soluble polyoxyalkylene glycols, appears to be totally unsuitable, both as a processing aid and as a plasticizer. Other compatible materials such as the diesters of the polyoxyalkylene glycols are suitable as plasticizers (they are considered "secondary" plasticizers in the P.V.C. art), but are not particularly helpful in improving M.V.T. It has been found generally preferable to use the polyoxyalkylene glycol diester type plasticizer when the starting material contains a polyester urethane.

The preferred practice of the method of this invention is as follows:

I. Formulating the Starting Material

A suitable polyurethane, i.e., one which will provide a film with a storage shear modulus of 4×10^7 to 5×10^8 dynes/cm.² and a loss tangent value of less than 0.5, determined at a frequency of 0.2 cycle/sec. and a temperature of 23° C., is combined with a suitable solid filler and, preferably, a suitable processing aid. A plasticizer can be included if desired. The resulting solid filler loading should be about 30 to about 60 percent, preferably 40-50 percent, by volume (by weight, the range of loading in parts of NaCl per hundred of polyurethane, i.e., phr., is about 125 to about 250 phr.). The processing aid is added in the amount of about 1 to about 10 parts per hundred of polyurethane, preferably about 3-8 phr. The plasticizer is added in the amount of about 1-20, preferably 5-15, phr. Suitable processing aids, plasticizers, and polyurethanes are described in detail subsequently.

The preferred fillers are leachable with water or aqueous media such as water containing a detergent. An example of such a filler is a finely divided inorganic salt. Typical inorganic salts are the sulfates or chlorides of potassium or sodium. Sodium chloride is fully operative in this invention and has obvious economic advantages, but generally speaking, any water-soluble material which remains solid and does not become degraded or enter into side reactions with the polyurethane at temperatures up to about 250° C. is suitable. The preparation of the film-forming mixture involves conventional steps and need not be described in detail. The filler should be pulverized to the point where it will consist of particles less than about 30 microns in size. Salt particles with an average longest dimension larger than 30 microns are useful in this invention, e.g., for intermediate layers; but for the top layer of a shoe upper material, 1-30 micron-size pores, and hence 1-30 micron salt particles, are preferable. In fact, salt particles smaller than 15 microns in size, especially those having an average longest dimension of about 5 microns, are preferred.

Although any suitable conventional process can be used to provide the starting material for the process of this invention, a preferred formulation method is as follows: Sodium chloride is blended with a small amount (e.g., 1-3 phr.) of anticaking agent. Suitable anticaking agents are salts of organic acids, particularly calcium stearate. The sodium chloride is pulverized to provide particles having an average size of less than 30 microns. These particles are then milled with small pellets of a suitable solid polyurethane elastomer and the processing aid and, if desired, the plasticizer. The milled salt-polyurethane composition is then ground and fed to a press, a set of calender rolls, or an extruder.

II. Heat Forming

An integral, salt-filled polyurethane film is formed from the starting material produced in step (I) by pressing, calendering, or extruding. The result is a smooth sheet material. The term "film" is used because, in this art, it frequently distinguishes preformed layers from coatings deposited on substrates. For example, "coatings" can be cast, knife coated, or sprayed from a liquid medium onto an adhering or nonadhering substrate. It should be noted, however, that the term "topcoat" is sometimes used in this art to denote the outermost layer of a shoe upper material regardless of whether this layer is a "film" or a "coating." To be consistent, the term "film" is used herein to denote an integral sheetlike material which can be bonded to, but which is formed separately from, a substrate.

III. Annealing

As pointed out previously, the heat-formed film is heat treated long enough and at a high enough temperature to relieve stress but not so long or at so high a temperature that degradation of the film results. Polarized light inspection of a transparent, salt-loaded polyurethane film before and after heat treatments conducted according to this invention shows definitely that the heat-treated film has been relieved of stresses. Hence, "annealing" is considered a suitable descriptive term for this heat treatment step. Suitable annealing temperatures vary with the type of polyurethane used. For the polyurethane materials suitable for use in this invention, ambient temperatures below about 250° F. (about 120° C.) are very inefficient insofar as relieving stress is concerned. Temperatures above 120° C. are therefore preferable, since relief of stresses can definitely occur, and the annealing will in fact be substantially complete, for the purposes of this invention, in an hour or less. To reduce the annealing time to a minimum, ambient temperatures up to about 500° F. (260° C.) can be used. Temperatures above 260° C. rapidly degrade most polyurethane-containing materials. The degradation can be quite serious if the duration of such high-temperature heating lasts for as little as several seconds. At 260° C. and below, however, little degradation is likely to occur if the heating lasts only seconds, particularly with polyester urethanes. In short, the preferred annealing range is about 250°–500° F., and the preferred time is about 5 seconds–60 minutes. In the case of the preferred polyesterurethane starting materials, optimum annealing conditions are 350°–425° F. (180°–220° C.) for 1–10 minutes. Preferably no pressure is applied to the film during the annealing step, only heat, although slight pressure less than about 10 p.s.i. is not detrimental. Ordinarily the film to be annealed is merely laid on a nonadherent support around which hot air is circulated or over which radiant heaters are placed. If the unannealed film is heat formed by pressing, and annealing is performed in the same equipment module, the pressure should be at least partially relieved during the annealing step. In any event, heat forming must be complete prior to annealing.

IV. Embossing

The leatherlike appearance of a microporous film made according to this invention is substantially enhanced by various embossing techniques. Although the embossing step preferably follows the annealing step and precedes the leaching step, described hereinafter, embossing can be carried out at any suitable point in the process of my invention. For example, embossing can precede the annealing step, particularly when the preservation of fine detail in the embossed surface is not important. Embossing can follow the leaching step if preservation of M.V.T. is not important; obviously this latter alternative is not preferable for the preparation of men's shoe upper material. It is within the scope of this invention to carry out the embossing operation either simultaneously and/or in the same equipment module with other steps of the process of this invention, e.g., heat laminating. The annealing step can likewise be carried out in the same equipment module as the embossing step, but, for maximum annealing, not at the same time, due to the differences in conditions between the two steps.

The embossing conditions are preferably tailored to facilitate processing of the film and to preserve its leatherlike properties (M.V.T., flex life, scuff resistance, etc.).

A preferred method of embossing is to use a platelike member or a roll with a pattern thereon which resembles natural leather. The plate or roll is pressed against the surface of the salt-filled film in the desired temperature and pressure ranges to achieve accurate replication. Needless to say, it is within the scope of this invention to emboss the film such that it will have any desired grain or a smooth surface capable of taking a high polish. The exact character of the embossing, so long as it does not interfere with the aforementioned leatherlike properties, is a matter of choice for the skilled artisan.

When plate embossing is used, the peak temperature obtained during the course of the embossing period (which

preferably lasts 5 to 30 minutes) is up to about 300° or 350° F. (about 150° or 180° C.). Pressures as low as 10–16 p.s.i. provide good detail. When continuous roll embossing is used, the temperatures are somewhat similar but the available time is less. (The pressure is applied only while the film is in the nip.)

V. Leaching

The finely divided filler, as pointed out previously, is preferably a water-soluble inorganic salt such as the chloride or sulfate of a suitable metal, e.g., sodium or potassium. For economic reasons and for its inertness toward polyurethanes, water is the preferred solvent used in this leaching step, with or without the addition of detergents. The solvent can be at any suitable temperature. Elevated temperatures (e.g., 25°–100° C.) can reduce the leach time. The solvent can partly be employed in the gas phase, e.g., as steam/water mixtures.

The void volume obtained by leaching is essentially determined by the volume percent of filler in the salt-loaded film. The previously mentioned filler loadings provide a leached film with a good M.V.T., good scuff resistance, and a long flex life.

Although any polyurethane which meets the G' and loss tangent requirement of this invention can be used, it is preferred to use substantially linear polymers containing -NH-R-NH-CO- and -X-Z¹-X-CO- units, and -X-Z²-X-CO- units in the polymer chain, wherein R is an aliphatic or aromatic group (e.g., Ar, as defined previously); X is O, S, NH, N-aliphatic, or the like; Z¹ is a polyoxyalkylene or polyester chain; and Z² is a divalent aliphatic or aromatic radical. Although these units are shown as divalent structures, it should be understood that, if a cross-linked polyurethane is desired, the "Z¹," "Z²" or "R" groups would have one or more additional substituents. The Z² radical is derived from a compound having the formula Z²(XH)_m, wherein Z² and X are as defined previously, m is 1–5, preferably 2 or 3, and H is an "active hydrogen" as defined in the Zerwitoff test, J. Amer. Chem. Soc. 49, 3181 (1927). In the preferred polyurethanes, X is O and R is Ar, as defined previously. If the Z¹ chains in the molecule are not the same, i.e., the polymer contains more than one kind of polyoxyalkylene and/or polyester chain, at least one Z¹ chain preferably has a molecular weight of at least about 400 but less than about 3,000.

When Z¹ is a polyester chain, the polyester units are preferably of the repeating formula -O-A¹-O-CO-A²-CO-, wherein A¹ and A² are divalent aliphatic groups such as alkylene radicals. These polyester units are derived from the interaction of a bifunctional initiator with one or more lactones, for example, as described in U.S. Pat. No. 2,933,477, or by an esterification or ester-interchange reaction involving a dicarboxylic acid or anhydride or ester thereof with an alkylene polyol, preferably an alkylene glycol. The bifunctional initiators referred to previously are compounds having two reactive sites capable, with or without the aid of a catalyst, of opening a lactone ring and forming an open chain of repeating ester units. Examples of useful initiators include the lower alkylene glycols (e.g., ethylene glycol, propylene glycol), alkanol amines such as ethanol amine, and alkylene diamines. Suitable lactones include the omega-C₅-C₈ lactones, e.g., epsilon-caprolactone, epsilon-methyl-epsilon-caprolactones, and zeta-antholactone. Especially suitable polyester chains in the 300–3,000 molecular weight (preferably 800–1,200) range can be obtained from epsilon-caprolactone and ethylene glycol.

When polyesters are prepared from dicarboxylic acids, anhydrides, or esters, and alkylene glycols, the preferred acid, anhydride, or ester, can be selected from a wide variety of polybasic (preferably dibasic) acids. To facilitate extrusion of the ultimate polyurethane, it is preferred to use the dibasic fatty acids, i.e., HOOC-(CH₂)_n-COOH, wherein n is a small integer, e.g., 1–8. Particularly suitable dibasic acids are malonic, succinic, and adipic. Examples of useful alkylene polyols are ethylene glycol; 1,3-propane-diol; 1,4-butane diol, and the like. Especially good results are obtained when the polyester chain contains 1,4-butylen adipate units.

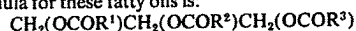
The preferred polyurethanes of this invention are prepared by mixing a molten hydroxyl terminated polyester or polyether and a molten arylene diisocyanate with a small amount of alkylene glycol; see, e.g., U.S. Pat. 2,871,218. The resulting reaction, particularly when a polyester glycol is the polymeric glycol reactant, is fairly rapid, and a catalyst is not generally required. Alternatively, known techniques involving the use of a prepolymer can be used. In those instances where a catalyst can be helpful, particularly when a polyetherglycol (e.g., polytetramethylene ether glycol, polypropylene glycol, etc.) is the coreactant, any suitable prior art catalyst can be used. The use of hydroxyl-terminated polyesters as opposed to carboxyl-terminated polyesters is preferred because of the difficulties attendant upon carbon dioxide formation which would result from an NCO/COOH reaction. The use of polyesters and/or polyethers containing saturated rather than olefinic radicals is preferred in order to avoid the presence of unwanted sites for cross-linking.

It is permissible to modify the stiffness of the polymer by including in the polyurethane-forming reaction other chain-extending, chain-branching, or chain-terminating agents, e.g., arylene diamine chain extenders. Preferred chain-branching agents are the triols and triamines commonly used in the polyurethane art. Various monoamines and monohydroxy compounds are known in the art for use as chain-terminators. Chain propagation can be carried out in any suitable manner known in the art, e.g., including these hydroxyl- or amine-containing compounds in a "one shot" mixture (generally along with a catalyst) or interacting the chain extenders with a suitable prepolymer. Since the polyurethane films of this invention are made by a heat-forming step, the more heat-resistant polyurethanes are preferred. A good heat-resistant polyester urethane which also provides films with good G' and loss tangent measurements is derived from a reaction mixture comprising hydroxy-terminated poly(1,4-butylene adipate), 1,4-butane diol, and diphenyl methane-p,p'-diisocyanate.

Suitable commercially available polyurethanes are available from B. F. Goodrich Chemical Co. under the trade names "Estane" 5701-F1 and 5707-F1 (polyester urethanes) and "Estane" 5714 (a polyetherurethane).

Although the polyester urethanes are easier to use in this process in some respects, they may lack the desirable low-temperature flex properties of the polyetherurethanes. It is, however, possible to improve the low-temperature properties of the polyester urethanes by blending them with a plasticizer which will not detract from other desirable properties, e.g., the M.V.T. of a microporous film, the scuff resistance, etc. It is difficult to predict such undesirable side effects. It has been found that diesters of polyoxyalkylene glycols which are substantially water-insoluble appear to meet the exacting criteria of this invention. Examples of such plasticizers are poly(ethylene glycol)-di-alkanoates such as tetraethylene glycol di(2-ethylhexanoate), available from Union Carbide Corp. of New York, N.Y. as "Flexol 4GO." This plasticizer is not a substitute for the "processing aid" of the invention, however. It is preferable to use at least 3 parts per hundred parts (by wt.) polyurethane of the processing aid even if the plasticizer is included in amounts up to about 20 parts per hundred.

The preferred class of processing aids are the epoxides of fatty oils (glyceryl esters of long-chain carboxylic acids), the fatty oils preferably being the unsaturated type. Suitable fatty oils are obtained from vegetable sources known as the "linolenic acid group," since these sources (soybean, candlenut, linseed, hemp or grapefruit or orange seed, English walnut, wheat germ, etc.) provide glyceryl esters of a group of fatty acids which includes a significant amount (e.g., 9 percent or more) of linolenic acid, a triolefinic C₁₈ carboxylic acid. The formula for these fatty oils is:



wherein R¹, R², and R³ are C₆-C₂₄, primarily C₁₂-C₁₈, saturated and unsaturated aliphatic radicals, particularly C₁₆ and C₁₈ alkenyl, alkadienyl, and alkatrienyl radicals. Epoxidation occurs at least at one of the double bonds in these aliphatic

radicals, thus providing, in the case of epoxidized soybean oil, a class of compounds in the 850-1,100 (calculated theoretical) molecular weight range which freeze at about 0°-10° C., have an iodine number ranging from about 0.6 to about 17, an acid number (mg. KOH/g.) ranging from about 0.1 to about 0.7, a hydroxyl number of about 15 to about 21, an epoxy equivalent weight (see Durbetaki, Analytical chemistry 28, 2000 [Dec., 1956]) of about 230 to about 280, and a saponification number (grams saponified by 1 L. of 1 N KOH) of about 305 to about 320. Rohm & Haas Company of Philadelphia, Pa. supplies epoxidized soybean oil under the trade mark "Paraplex" G-60, G-61, and G-62. "Paraplex G-62," which freezes at about 5° C., has an average molecular weight of about 1,040, an iodine number of about 0.8, an acid number of about 0.6, a hydroxyl number of about 20, and an epoxy equivalent weight of about 237 is generally preferred. "Paraplex G-62" has an elemental analysis of 71.3 percent C/10.4 percent H. The percent of oxirane oxygen is 6.75 percent. "Paraplex" G-60 and G-61 have somewhat similar molecular weights, elemental analyses, epoxy equivalent weights, characteristics, and freezing points; they also contain both epoxy groups and carbon-carbon double bonds.

A leatherlike shoe upper material suitable for use in making quality men's shoes can be made by incorporating the process steps of this invention in an overall synthetic leather manufacturing operation. An example of how this can be done is schematically illustrated in FIG. 1 of the drawing.

From FIG. 1, it can be seen that a salt/polymer mixture (an inorganic salt such as sodium chloride, pulverized to a size suitable for providing microporosity, milled with pellets of a suitable polyurethane polymer—several suitable polyurethanes can be made or purchased in, for example, dry pellet form) is fed to heat-forming equipment, such as a press or a set of calender rolls, or, alternatively, ground first and then extruded. Preferably extruding or calendaring is used; the result in any event is a salt-loaded polyurethane film. The film can be first embossed and then annealed and, if desired, heat-laminated to a suitable substrate such as a woven (e.g., cotton) cloth and/or a second microporous or macroporous polymeric film. Preferably the heat-formed film is annealed, heat-laminated to the substrate, and embossed to provide a film having a leatherlike surface. The brackets of FIG. 1 indicate that the annealing, heat-laminating, and embossing steps can be combined in various ways. For example, the annealed film can be "lam-bossed" to a substrate. If the aforementioned woven or film substrate or substrates are omitted, the heat lamination step is, of course, omitted. If one or more film substrates are used along with or in lieu of a cloth substrate, the interposed films must be porous but need not be free of visible (<30 micron-size) pores, since it is covered up by the topmost, heat-formed, salt-loaded film. In fact, a substrate or interlayer (interposed) film having at least some 30-200 (preferably greater than 40) micron-size pores is preferred. This interlayer or substrate film can be provided in salt-loaded form and can be leached along with the top film; its composition can be similar to that of the top film, except that the salt loading can be much higher, since the interlayer will not suffer abrasion. The use of more and/or grosser pores in the interlayer appears to contribute to a more leatherlike "break" in the composite final product, and also helps to reduce the tendency to delaminate during flexing of the composite product.

As is well known in the art, it is frequently desirable to superpose a leatherlike film upon a nonwoven fabric substrate to provide a material with "flesh" and "grain" surfaces. See, for example, example 8 of U.S. Pat. No. 2,723,935. Webs or batts particularly suitable for use in this invention are random-laid, fibrous, sheetlike fabrics wherein the fibers are synthetic and are derived from organic polymers such as the polyamides, the polyesters, the polyolefins, the vinyl polymers, and the like. Natural fibers such as cotton are less preferred. The webs or batts can be needle punched and/or shrunken with heat to provide a dense, compact fibrous structure which can be im-

pregnated with a polymeric binder. The binder can be a solution or latex of a polyurethane, a poly(butadiene-styrene), or the like. After the conventional drying and finishing steps, the compacted nonwoven web or batt is ready to be combined or laminated with the salt-filled polyurethane film which may be already bonded to a woven or porous film substrate. Various methods of bonding the web or batt to the film or film/substrate composite can be used, among them the use of an adhesive interlayer which will not interfere with moisture vapor transmission, e.g., a layer of macroporous and/or microporous polyurethane adhesive. Regardless of how the web or batt is combined with the salt-loaded film or film/substrate composite, the next step is leaching the salt from the film and from any other layer or layers which are also salt-loaded (e.g., a second salt-loaded film as described previously). The leaching step provides the microporosity essential for good M.V.T. (The web or batt substrate is a porous fabric structure and has no adverse effect upon M.V.T.) After a number of suitable finishing steps, including drying, dyeing, sanding, polishing, and the like, a leatherlike sheet material comprising a microporous film superposed upon the web or batt is obtained. The characteristics of this sheet material are described subsequently. This material is particularly suitable for use in making uppers for men's shoes in the medium-to-high price range.

The annealing step of this invention can be carried out using any convective or radiant heating means which will not introduce strains into the film, e.g., an oven heated by hot air or other gases, infrared energy, or the like. For economical operation, this annealing step, and all the other steps shown or described in this application can be arranged into a continuous process. In such an operation, the salt-loaded film is continuously extruded or calendered onto a nonadhering, moving carrier or support such as an endless belt. The film is then annealed by passing the carrier at a controlled speed through, for example, a hot air oven.

A preferred form of the aforementioned leatherlike sheet material of this invention is described in FIG. 2. The composite material 10 preferably comprises a top layer 12 containing only micropores 16 and having an exposed "grain" (preferably embossed) surface 11 and an M.V.T., prior to the final finishing steps of 3,000–4,500 g./hr./100 m.² at 100 percent/50 percent relative humidity (R.H.); a backup (interposed) interlayer 13 which can be a woven cloth or, in this case, an interposed polyester urethane film containing at least some macropores 17; a nonwoven web 15 to provide a "flesh" side 18 for the product; and an adhesive interlayer 14 or the like bonding the backup interlayer to the nonwoven web. The adhesive layer 14 must be porous and can also contain macropores 17. Additional layers (not shown) can be sandwiched between top layer 12 and nonwoven web 15, if desired. All M.V.T. determinations herein are at 23° C.

After the final finishing steps (including dyeing, polishing, etc.), the M.V.T. of a material such as that illustrated in FIG. 2 has decreased, but is still above 1,500 g./hr./100 m.² at 100 percent/50 percent relative humidity (R.H.). With optimum processing conditions and ingredients, an M.V.T. above 2,000 g./hr./100 m.², also at 100 percent/50 percent R.H., is obtained. The flex life of the finished product exceeds 250,000 flexes (e.g., cycles of a Bally Flexometer) at 23° C. The abrasion loss is quite small. With an H-22 wheel and a 1,000 gram weight, the Taber Abraser removes less than 0.07 gram from the top layer 12 after 200 cycles (about 3 minutes). In fact, the abrasion loss, under these same conditions, is less than 0.045 gram with the preferred products. If top layer 12 were delaminated and tested, its loss tangent would still be less than 0.5, preferably less than 0.2, measured at 0.2 cycle/sec. and 23° C. Its G', however, would be lower—but still above about 10⁷ dynes/cm.². If the top layer were both delaminated and hot pressed to a nonporous film, its G' would be brought substantially back to the starting material range, i.e., above about 4×10⁷ dynes/cm.². The G' and loss tangent values, both of starting materials and final products, are preferably deter-

mined on films containing by weight, 1–10 parts per hundred (phr.) of epoxidized soybean oil. The exclusion of 1–20 phr. tetraethylene glycol (2-ethyl hexanoate) affects the loss tangent and G' values, but not substantially. The water leach step removes very little of either of these additives—both are substantially water insoluble.

The preferred polyurethane starting materials of this invention, when heat-formed to nonporous films containing the epoxidized soybean oil (e.g., "Paraplex" G-62), have the following properties: G'—0.5 to 2.5×10⁸ dynes/cm.², and loss tangent—0.05 to 0.2, at 0.2 cycles/sec.; G' and loss tangent taken at 23° C.

As pointed out previously, an important feature of this invention is the ability to directly control the thickness of the microporous film or films, the number, size, and distribution of the pores, and hence the void volume as well. The pores in the leached film will be substantially like the salt particles that were removed by leaching—in number, size, distribution, and even in shape. (Leaching out the face-centered cubic salt particles tends to leave behind pores which are roughly spherical or even roughly cubical in shape.) Thus, the void volume of films made microporous according to this invention ranges from about 30 to about 60 percent, preferably 40–50 percent.

The caliper (gauge or thickness) of these microporous films will not vary substantially over long lengths of film. The heat-forming step of this invention is preferably used to provide 5–30 mil. (125–750 micron) salt-loaded films. Any desired thickness of film can be made by this heat-forming step, and, unlike casting methods, making salt-loaded films greater than 5 mils (125 microns) in thickness and of uniform caliper poses no problem. Films of 3–5 mils (75–125 microns) thickness can also be heat-formed, but control of caliper is more difficult than with the thicker films. The upper limit of film thickness is dictated only by practical considerations of processing and fabricating. For example, films over 100 mils (2.5 mm.) thick could be made but would be less easy to work with than 3–100 mil films. Because careful milling of the salt and polymer results in a uniform distribution of a known amount of salt particles of known size in a polyurethane matrix, the number of pores per sq. mm. of film surface can be controlled in a manner exactly analogous to the manner of controlling the pore size, void volume, etc. With 5-micron salt particles, for example, there will be 15,000–30,000 pores/mm.², depending on the salt loading. It is preferred to provide more than 500 pores/mm.², but more than 100,000 pores/mm.² is not absolutely necessary for good M.V.T.

The principle and practice of this invention is illustrated in the following examples wherein all parts are by weight, unless otherwise specified.

EXAMPLE I

The following materials were compounded on a two-roll rubber mill:

- 300 g. Polyester urethane pellets analyzed and found to have been derived from:
 - 1.00 mole poly(1,4-butylene adipate) glycol
 - 1.85 moles 1,4-butane diol
 - 2.85 moles diphenylmethane - p,p'-diisocyanate
 (These polymer pellets are available from B. F. Goodrich Chemical Co. under the trade designation "Estane 5707-F1.")
- 480 g. Sodium chloride powder, average particle size ground to 5 microns (Available from Morton Salt Co. as "Culinox 999 Grade" in 300–400 micron-size particles.)
- 480 g. Sodium chloride powder, average particle size ground to 5 microns (Available from Morton Salt Co. as "Culinox 999 Grade" in 300–400 micron-size particles.)
- 15 g. Epoxidized soybean oil, average molecular weight 1,040, iodine number 0.81, 6.75 percent oxirane oxygen, epoxy equivalent weight 237. (Available from Rohm & Haas Co., Philadelphia, Pa. as "Paraplex G-62").
- 5 g. Calcium stearate

The particular polyesterurethane described above was selected because of its preferred G' (about 2.2×10^8 dynes/cm.² at 23° C.) and loss tangent (about 0.1, determined at 23° C. and 0.2 cycle/sec.) properties.

The fine particle salt was prepared by ball milling in toluene in a porcelain ball mill for about 65 hours using ½ inch glass marbles. Compounding required about 8 minutes with a roll temperature of about 340° F. (about 171° C.). The batch was scraped off the roll, scored, and ground in a Sprout-Waldron cutter through a 3/16 inch screen to yield a granulated extruder feed having an average particle size of about ¼ inch (3 mm.) diameter. Several batches were prepared and mixed together to form a large master feed batch.

Extrusion was conducted in a machine having a 1¼-inch barrel diameter, a 24:1 length-to-diameter ratio, and using a 14 inch (36 cm.) die (Johnson Mfg. Co.) and a screw with a 2.5:1 compression ratio. The screw had twelve flights in the feed section, three in the transition zone, and nine in the metering zone. Flight depth was 0.85 inch (2.2 mm.) in the metering section. The screw had a pointed tip and no screen pack was used. The film was extruded at a screw speed of 44 r.p.m. resulting in a power consumption of 200 watts. Maximum barrel temperature was 445° F. (230° C.) and die temperature was 400° F. (205° C.). The film was extruded into takeaway rolls consisting of a silicone rubber roll and a cold water cooled chrome roll. Nip pressure was 20 p.s.i. A second pair of rolls pulled the film at a rate of 5.5 ft./min., resulting in a film thickness of about 12 mils (about 300 microns) and a width of about 13 inches (33 cm.). Output of extrudate was about 40 lbs. (about 18 kg.) per hour.

A sheet of extruded film about 13 inches × 18 inches (33×46 cm.) was placed on silicone-treated paper and thermally treated by placing it in a large Despatch forced air oven for 2 minutes. The hot air in the oven was kept at about 400° F. (205° C.). Next, samples were cut from the annealed and from the unannealed film for measurement of properties. Both samples were leached free of NaCl with distilled water heated to 40° C. M.V.T. rate for the samples was measured as follows: A 4-ounce jar half filled with tap water and with a hole in the lid was used as the testing apparatus for each sample. A circular sample was die cut and placed in the lid of the jar providing the barrier between the water vapor in the jar and the water vapor in the air outside. The assembly was weighed on an automatic balance and then placed in a room maintained at a relative humidity of 50 percent and a temperature of 23° C. After 24 hours in the room the test assembly was weighed again to determine the weight loss. From the weight loss, the exposed sample area, and the test time, the M.V.T. rate was calculated. Four samples each of annealed and unannealed film (all having been leached free of the NaCl powder with 40° C. distilled water) were tested at the same time and the results were averaged. The following results were obtained:

Sample	M.V.T. Rate (gms./hr./100 sq. meters)
Unannealed	1,850
Annealed	3,800

Measurements were also made of the percent by volume of voids in both annealed and unannealed films. The procedure was as follows: A circular sample was cut with a die having a diameter of 4.57 cm. Thickness was measured at 6 points to 0.1 mil accuracy with an accurate micrometer. Sample volume was calculated. The sample weight was measured on an analytical balance and the sample density (i.e., apparent density) was calculated. Next the density of a film composition composed of 100 parts Estane 5707 F1, 5 parts "Paraplex G-62," and 1.5 parts calcium stearate was calculated by using the weighted value of the known density of each component. This density was 1.21 g./cc. and was the density of the microporous film material left after leaching out the salt. Next the void volume was calculated using the following derived equation:

$$\% \text{ voids by volume} = \frac{(1.21 - \text{sample density})}{1.21} \times 100$$

The theoretical void volume was determined from the calculated volume of salt leached out. The following results were obtained:

Sample	Measured	% Voids	Theoretical
Unannealed	44.7%		45.7%
Annealed	44.7		45.7

Thin sections of both annealed and unannealed films were prepared by first imbedding small samples in an epoxy resin, freezing, and then cutting 5-micron sections with a microtome. The samples were examined under 500 magnification with a light microscope. Photographs were made of the structures and pictures were printed under a twofold enlargement resulting in a total magnification of 1,000 times for the structures. Clear, detailed pore structures were observed in each sample, with no differences discerned between the annealed and unannealed films.

The annealed film was pressed to a nonporous layer to determine its physical properties after processing, which were: G' : 2.18×10^8 dynes/cm.²

Loss Tangent: 0.10 These measurements indicate that the degradative effect of heat-forming (in this case extruding), annealing, and leaching upon the polyesterurethane was not very substantial.

EXAMPLE II

Three batches (A, B, and C) of extruder feed were prepared according to example I, but with 540 g. (180 phr.) of the salt. Further modifications were: In Batch A, 15 grams (5 phr.) of tetraethylene glycol di(2-ethylhexanoate) were included in the formulation; in Batch B, 30 grams (10 phr.) of this diester were included. In all other respects, the three batches were identical to the formulation of Example I.

The extruder used in this example had a constant flight depth of 250 mils (6.4 mm.) and a 2:1 compression ratio. The screw speed was 60 r.p.m., the power consumption was 300 watts, and the maximum barrel temperature was 430° F. (220° C.). The extrudate was very slightly drawn to provide 6 ft./min. of a 15 mil (375 micron) film. The films were annealed as in Example I, and were made into finished microporous leather substitutes in accordance with FIG. 1 of the drawing, a woven cloth substrate being used in the heat-laminating step, and distilled water at 40° C. being used in the leaching step. All three samples were compared as to flex life, determined on a Bally Flexometer at 0° F. (-18° C.) and 23° C. All three samples had about the same flex life at 23° C. (greater than 250,000 cycles), but the Batch A and Batch B samples had more than double the flex life of the Batch C sample at -18° C. The M.V.T. value for each of the finished samples was determined as in Example I, all samples having an M.V.T. of 2,200 g./hr./100 m.². The M.V.T. values of portions of the annealed, leached films, tested prior to any finishing steps and separate from the cloth backing and nonwoven base web, were all 3,700 g./hr./100 m.².

As the person skilled in the art will appreciate, many modifications of this invention are possible. For example, the microporous films are useful in women's shoe uppers, inexpensive men's shoe uppers, shoe soles and liners, rainwear, upholstery, fabrics, hospital sheeting, wound dressings, etc., as well as in quality men's shoe uppers, the preferred use.

Physical measurements mentioned throughout this disclosure were taken at 23° C. unless otherwise specified. Annealing temperatures refer to environmental (ambient) conditions, unless otherwise specified.

What is claimed is:

1. A microporous film having a void volume of about 30 to about 60 percent, having 500-100,000 pores per square millimeter of surface, being free of visible pores, and comprising:

a thermoplastic polyurethane resin having a loss tangent less than 0.5 determined at 0.2 cycle/sec. and 23° C. and a storage shear modulus at 23° C. of about 4×10^7 to about 5×10^8 dynes/cm.²,

and about 1 to about 10 parts, per hundred parts by weight of said polyurethane, of an epoxidized glyceryl ester of a C₅-C₂₄ carboxylic acid, said epoxidized glyceryl ester being blended with said polyurethane.

2. Film according to claim 1 wherein said microporous film is 3-100 mils in thickness, has a void volume of 40-50 percent, and has 15,000-30,000 pores/mm.², said pores measuring less than 15 microns in their largest dimension, and wherein said epoxidized glyceryl ester is epoxidized soybean oil.

3. Film according to claim 1 wherein said microporous film contains a plasticizing amount of a substantially water-insoluble diester of a polyethylene glycol.

4. Film according to claim 3 wherein said diester is tetraethylene glycol di(2-ethyl hexanoate).

5. Film according to claim 1 wherein said microporous film is included in a laminate and is laminated to a backup interlayer, and said interlayer is in adherent contact with a nonwoven web.

6. Laminate according to claim 5 wherein said laminate of said microporous film, said interlayer, and said web has an M.V.T., when exposed to a relative humidity of 100 percent on one side and 50 percent on the other side, greater than 2,000 g./hr./100 m.², and a flex life in excess of 250,000 cycles; and wherein said microporous film, tested independently of said laminate, has a storage shear modulus of at least 10^7

dynes/cm.², said M.V.T., flex life, and storage shear modulus being measured at 23° C.

7. A laminar sheetlike leather substitute material, including, as laminae thereof, a microporous film and a nonwoven web, said microporous film having: a storage shear modulus greater than 10^7 dynes/cm.²; a void volume of about 30 to about 60 percent; a porosity of about 15,000 to about 30,000 pores/mm.² of surface, said pores being less than 15 microns in their widest dimension; and a thickness of 3-100 mils; said microporous film comprising:

a polyurethane having a loss tangent less than 0.2 determined at 0.2 cycle/sec. and 23° C. and a storage shear modulus at 23° C. of about 4×10^7 to about 5×10^8 dynes/cm.², and

about 1 to about 10 parts, per 100 parts by weight of said polyurethane, of epoxidized soybean oil.

8. A porous polymeric film comprising:

1. a polyurethane containing (a) -NH-R-NH-CO- units, wherein R is selected from the group consisting of an aromatic and an aliphatic group, and (b) O-Z-O-CO- units, wherein Z is selected from the group consisting of a polyoxyalkylene and a polyester chain, and

2. a film-formation-facilitating amount of an epoxidized glyceryl ester of a C₅-C₂₄ carboxylic acid, said epoxidized glyceryl ester being blended with said polyurethane.

9. A porous polymeric film according to claim 8 wherein said film-formation-facilitating amount is about 1 to about 10 parts per 100 parts by weight of said polyurethane.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,640,829 Dated February 8, 1972

Inventor(s) Robert L. Elton

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 41, "adaption" should be -- adaptation -- .
Column 6, line 67, "preformed" should be -- pre-formed -- .
Column 12, lines 67-69, under EXAMPLE I, should be deleted.
These three lines are a duplication
or repeat of lines 64-66 just preceding.
Column 13, line 19, "0.85 inch" should be -- 0.085 inch -- .
Column 16, line 21 (in Claim 8), after "(b)" insert a
hyphen, so that the formula reads
-- -O-Z-O-CO- units, -- .

Signed and sealed this 8th day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTESCHALK
Commissioner of Patents

EXHIBIT C

United States Patent [19]

Elton et al.

[11] 3,870,593

[45] Mar. 11, 1975

[54] STRETCH-ORIENTED POROUS FILMS AND PREPARATION AND USE THEREOF

[75] Inventors: **Robert L. Elton**, White Bear Lake;
John F. Vander Louw, Woodbury,
both of Minn.

[73] Assignee: **Minnesota Mining and Manufacturing Company**, St. Paul,
Minn.

[22] Filed: **Apr. 29, 1974**

[21] Appl. No.: **465,273**

Related U.S. Application Data

[62] Division of Ser. No. 260,321, June 6, 1972, Pat. No. 3,844,865.

[52] U.S. Cl. 161/159, 161/160, 161/167,
161/190, 161/402, 161/DIG. 2, 260/2.5 AY

[51] Int. Cl. B32b 3/00, B29c 17/02

[58] Field of Search 161/159, 160, 167, 190,
161/402, DIG. 2; 260/2.5 AY

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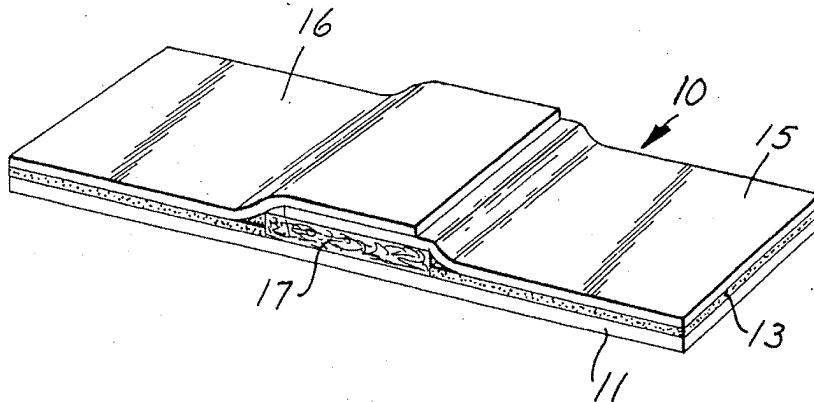
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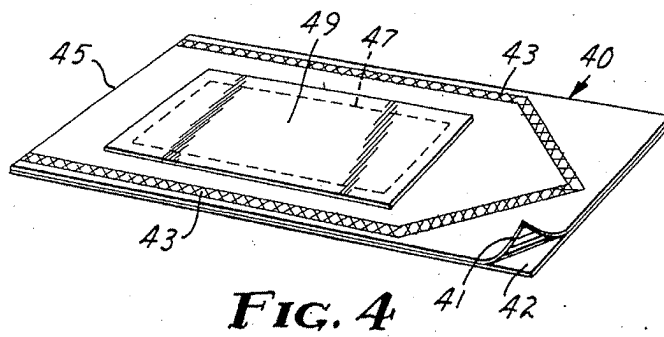
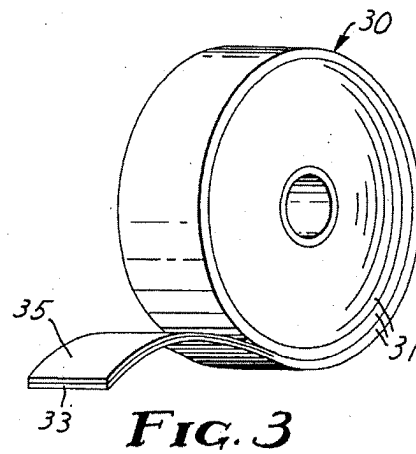
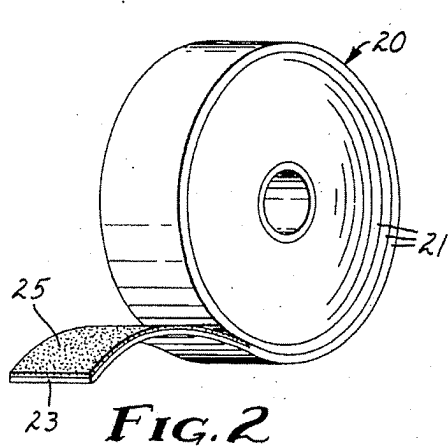
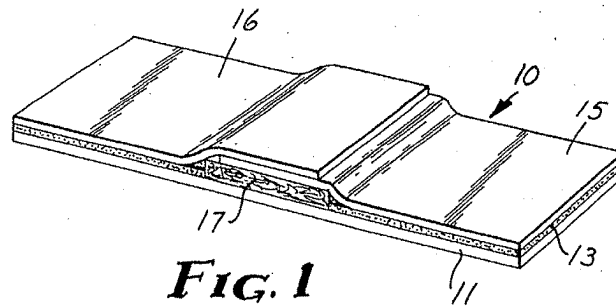
Primary Examiner—William J. Van Balen
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DeLaHunt

[57] ABSTRACT

Porosity (preferably microporosity) can be introduced into a polymeric film by (1) dispersing finely divided particles of a non-hygroscopic inorganic salt such as calcium carbonate into a suitable polymer, e.g., by milling, (2) forming a film of the filled polymer, and (3) stretching the film to provide good porosity and water absorptive or transmissive characteristics. It is unnecessary to leach out the particles of the inorganic salt, and the resulting porous film is useful in laminates, adhesive tapes, gas permeable containers, first aid dressings, and the like even though it still contains these particles.

6 Claims, 4 Drawing Figures





STRETCH-ORIENTED POROUS FILMS AND PREPARATION AND USE THEREOF

This is a division of application Ser. No. 260,321, filed June 6, 1972 now U.S. Pat. No. 3,844,865.

FIELD OF THE INVENTION

This invention relates to porous (preferably microporous) films made from suitable polymers and articles of manufacture (laminates, adhesive tapes, permeable containers, first aid dressings, etc.) made from the porous films. An aspect of this invention relates to the incorporation of a pore-forming or nucleating non-hygroscopic particulate material into the polymer prior to formation of the film, which particulate materials remain in the film after the film is made porous. Another aspect of this invention relates to a method for introducing porosity into a filled polymeric film without leaching out or otherwise removing the filler. Another aspect of this invention relates to the utilization of particular pore-forming or pore-nucleating agents in the manufacture of microporous polymeric films and the utilization of the films in various fabricated products.

DESCRIPTION OF THE PRIOR ART

It is known that microporous films can be made by mixing a leachable filler with a polymeric material, forming the filled polymer into a film, and leaching the filler from the film with water or a suitable solvent for the filler. A recently-developed example of this technique is described in U.S. Pat. No. 3,376,238 (Gregorian et al.), issued Apr. 2, 1968. See also British Pat. No. 1,126,849, published Sept. 1968, and British Pat. No. 1,051,320, published Dec. 1966. The resulting leached film contains micropores, i.e., pores smaller than about 25 microns, and can be capable of transmitting water vapor, a property known as water vapor permeability or "moisture vapor transmission" (hereinafter referred to as "MVT"). It has been found that stretch-orientation of a sodium chloride-filled film prior to leaching out of sodium chloride with water improves the water vapor permeability. See British Pat. No. 844,801, published Aug. 17, 1960. The water- or solvent-leach step can be quite lengthy, and it is difficult to be sure that all traces of the filler have been removed. It would simplify the prior art processes greatly if the leach step could be omitted.

The selection of a filler can also pose problems. Organic, solvent-soluble or water-soluble fillers are generally expensive and subject to degradation by heat (and possible side reactions with the polymer), while inorganic water soluble fillers such as NaCl and NaBr tend to be hygroscopic, have a caking tendency which makes them difficult and/or wasteful to handle, and are difficult and expensive to obtain in pure and/or finely-divided form. The ideal filler would be inorganic, high-melting, non-hygroscopic (i.e., less hygroscopic than pure or commercial grade NaCl) easily purified, easily pulverized, abundant, inexpensive, and free of caking tendencies. Such fillers exist, e.g., calcium carbonate, but are water insoluble. They can be leached out with acids, e.g., aqueous HCl, but it is undesirable to expose a polymeric material to strong acids and bases, and the gas formed (CO₂) from the reaction with HCl could impede the leaching and cause extremely low leach rates. Furthermore, an acid leach step generally creates the need for a second leach step with pure water, as is

shown in Examples 2, 3, 5, and 6 of British Pat. No. 1,126,849. Thus, calcium carbonate or the like is commonly used as a filler which has no pore-forming function, as in the products described in U.S. Pat. Nos. 3,245,942 (Limperos), issued Apr. 12, 1966, and 3,154,461 (Johnson. calcium carbonate is also used as an additive to solvent cast microporous films; see U.S. Pat. No. 3,496,001 (Minobe et al.), issued Feb. 17, 1970. It has been suggested that pores can be formed without a leaching step by including a milled elastomer in a polymer matrix and stretching the filled matrix. See U.S. Pat. No. 3,407,253 (Yoshimura et al.). However, this technique can be difficult to control, at least in terms of the size and shape of the resulting pores. Furthermore, the milled elastomer lacks the previously described advantages of an inorganic filler such as calcium carbonate. The use of a pore-nucleating agent is omitted completely in the process described in U.S. Pat. No. 3,558,764, issued Jan. 26, 1971, but this process involves a multitude of steps which are necessary in the present invention.

Calcium carbonate has been used as a filler in the solvent/nonsolvent method of producing microporosity (see U.S. Pat. No. 3,555,129, Jan. 12, 1971), but merely as a means for facilitating the leaching out of the solvent, not to eliminate a leaching step.

Accordingly, this invention contemplates porous (preferably microporous) films made by stretch-orientation of a filled polymeric matrix wherein the filler is not leached from the film, yet serves as a nucleating agent for forming pores during the stretch orientation step. This invention further contemplates microporous films made by a stretch orientation technique wherein a nucleating agent forms pores during the stretch orientation step, and this nucleating agent is inorganic, high-melting, non-hygroscopic, easily purified, abundant, inexpensive, free of caking tendencies when handled in bulk quantities, and commercially available as particles having a suitable fine degree of subdivision, e.g., averaging less than 15 microns in diameter. This invention also contemplates products derived from these microporous films, e.g., laminates, adhesive tapes with porous backings, first aid dressings, gas- or steam-permeable bags or containers, and the like.

BRIEF SUMMARY OF THE INVENTION

Briefly, this invention involves (1) dispersing finely divided particles of calcium carbonate or the like into a suitable polymer by a milling step or the like, (2) forming a film of the filled polymer by a heat-forming process such as extrusion, calendering, or pressing, and (3) stretching the film to induce an interconnecting porous structure in the film, whereby the film is rendered porous (i.e., macroporous or microporous, preferably microporous) without removing the filler particles. It is not clearly understood why removal of the filler particles is unnecessary. Although this invention is not bound by any theory, it is believed that the polymer matrix separates from the filler particles during the stretching step, and upon release of tension, the relaxed matrix does not completely return to its original shape. This incomplete relaxation or return results in micropores which are larger than the enclosed filler particles. Surprisingly, the enclosed filler particles do not substantially interfere with the permeability of the porous film. In fact, the moisture vapor transmission (MVT) of the porous film is not measurably improved by leaching

out the CaCO_3 filler with aqueous acid or the like. This observation is difficult to explain, particularly since the prior art (e.g., Britist Pat. No. 844,801) clearly calls for a leaching step. The elimination of the leaching step and the ability to use fillers such as calcium carbonate result in a process which provides a porous film of polymer at very nearly the same cost as non-porous films of similar thickness. Apparently, the pores formed by the process of this invention are not closed cells and are somehow interconnected. This, too, is difficult to explain, but is apparently due in some measure to the effects of stretch orientation combined with the amount, number, and size of calcium carbonate particles. There is some evidence to indicate that moisture or gases passing through films of this invention normally have to pursue a tortuous path of relatively large cavities connected to each other by submicron sized openings or passages, as will be explained subsequently.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of an adhesive first aid dressing utilizing a microporous film of this invention as the adhesive tape backing.

FIG. 2 is a perspective view of a pressure-sensitive adhesive tape roll, wherein the backing is a film of this invention.

FIG. 3 is a perspective view of a roll of burn dressing material wherein the backing of the dressing is a film of this invention.

FIG. 4 is a perspective view of a heat-sealable, sterilizable bag utilizing a microporous film of this invention.

In FIG. 1, first aid dressing tape 10 is an adhesive tape having a backing 11, which is a microporous film of this invention, a pressure-sensitive adhesive coating 13, which has been made porous and which can be acrylate pressure-sensitive adhesive of the type disclosed in Ulrich U.S. Patent Re. 24,906, issued Dec. 1960, release liners 15 and 16, for protecting the adhesive layer prior to use, and a conventional absorbent (e.g., gauze) pad 17. When in place on the skin, moisture from the skin can pass through the adhesive coating 13 and through film 11 at a controlled rate. The ability of the dressing 10 to "breathe" in this fashion is beneficial to the skin.

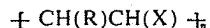
FIGS. 2 and 3 both illustrate films of this invention, 23 and 33, respectively, wound directly upon themselves around a central core forming a plurality of overlapping convolutions, 21 and 31, respectively, thus providing conveniently stored rolls 20 and 30 which can be unwound to provide desired lengths of film 23 and 33. Film 23 is coated on its inner major surface with a pressure-sensitive adhesive 25 which does not delaminate or offset as the tape is unrolled. Rubber-resin or acrylate pressure-sensitive adhesives can be used as adhesive 25, and the adhesive can be made porous, if desired. Since film 23 is porous, it can transmit moisture or gases as does first aid dressing 10 of FIG. 1. Film 23 also accepts liquid or solid deposits and can serve as a writing surface for oleaginous or alcohol and/or water-based inks or writing fluids or graphite pencil marks. Film 23 can thus be provided with printed matter on its uncoated major surface so that it can serve as a label tape. Film 33 of FIG. 3 is laminated to a non-adherent, moisture transmissive burn covering material 35. Thus, the film/covering composite (33 and 35) can be unrolled, cut to the desired length, e.g., with strips of porous adhesive tape from tape roll 20. The thus-bandaged burn area is permitted to transmit moisture

at a controlled rate through film 33, with significant beneficial effects upon the healing of the burn.

FIG. 4 illustrates a typical configuration for a bag 40 for surgical instruments or other medical devices or the like which can be sterilized in a gas (e.g., ethylene oxide) sterilizer or, if suitably heat-resistant, in a steam autoclave. Bag 40 is made two opposed sheets of non-porous polyethylene film 41 and 42 (or other heat sealable polymer, e.g., polypropylene, polyester, etc.), which form a package after being heat treated around all but one side of their peripheries, i.e., end 45, to form a 3-sided "chevron" type peelable heat seal area 43. Although polyethylene film can be heat bonded to itself to form a peelable heat seal, an adhesive seal area on one or both plies can be also used; see, for example, U.S. Pat. No. 3,217,871 (Lee) issued Nov., 1965. The object to be sterilized and stored is inserted through open end 45 and the heat seal area 43 is then extended by applying heat across end 45. Bag 40 is then ready for sterilizing. To permit entry and exit of sterilizing gas, a filter panel 49 of porous polypropylene film of this invention is laminated to the periphery 47 of a rectangular opening in film 41. The object (e.g., dressing or surgical instrument) which has been sealed in bag 40 and sterilized therein can then be stored in sterilized condition until the bag is cut or peeled open by the physician or nurse. The effective diameter of the pores of filter panel 49 is small enough (e.g., less than 0.5 micron) to serve as an effective barrier for bacteria, but not so small as to prevent entry and exit of sterilizing fluid, e.g., steam or ethylene oxide gas.

DETAILED DESCRIPTION AND EXAMPLES

The teachings of this invention can be utilized to provide porous films from a wide variety of film-forming polymeric materials, preferably of two diverse types: (1) stretch-orientable, non-elastomeric, at least partially crystalline polymers derived from polymerization of one or more unsaturated monomers and (2) stretch orientable polyurethanes. Among the non-elastomeric, crystalline-type polymers, it is preferred to use extrudable polymers having the formula



where n is the index of polymerization and X is hydrogen, lower alkyl (e.g., methyl or ethyl), halogen, $-\text{O-COR}'$ where R' is lower alkyl or aryl, hydroxyl, nitrilo, an aromatic group, an ester group, or the like and R is hydrogen, lower alkyl (e.g., methyl or ethyl), halogen, or the like. Typical members of this class of polymers can be made from one or more unsaturated monomers such as vinyl chloride or other vinyl monomers; vinylidene chloride or other vinylidene monomers; ethylene, propylene, 1-butene, and similar mono-unsaturated or poly-unsaturated hydrocarbons, acrylic monomers (e.g., acrylonitrile); styrene, etc. Thus, copolymers, terpolymers, etc., are also contemplated as are conventional modifications and chemical, physical, and radiological after treatments. Other modifications, e.g., plasticizing with conventional plasticizers (including the dialkyl phthalates and sebacates, the epoxidized soybean oils, etc.) are also permissible and generally preferable with relatively brittle materials such as polyvinylchloride (PVC). For most uses of microporous films, it has been found that the polyolefins, particularly polypropylene, are the preferred class of crystalline or partially crystalline stretch orientable polymers,

while olefin, conjugated olefin, vinyl arene, and ethylene-vinyl acetate polymers are least preferred. Some of the rubbery or elastomeric A-B-A block copolymers and ethylene-vinyl acetate copolymers have been found to be somewhat resistant to the porosity-inducing techniques of this invention. The above-described polymers can also be mixed, and mixtures of polyethylene and polypropylene (e.g., 2:1 polypropylene: polyethylene) are particularly useful. Another preferred class of polymers includes a wide variety of conventional polyurethanes, e.g., extrudable elastomers of the polyetherurethane or polyesterurethane type, which can be elastomeric. The elastomeric polyurethanes are preferably stretch oriented at elevated temperatures, e.g., 90°–150°C. The term elastomeric is used herein in accordance with the ASTM definition: "a material which at room temperature can be repeatedly stretched to at least twice its original length and upon immediate release of the stress will return with force to its approximate original length" is an "elastomer."

Other less preferred polymers include the polyesters (e.g., polyethylene terephthalate), the nylons, the perfluorinated olefins (polytetrafluoroethylene, polytrifluorochloroethylene), etc.

The principal requirements to be met in selecting a suitable urethane-type polymer or a suitable crystalline or semi-crystalline, non-elastomeric polymer are physical rather than chemical. The polymer should be capable of being "heat formed" (i.e., extruded, calendered, or pressed), without significant degradation, into a thin (less than 2 mm, preferably less than 1 mm) film. After film-formation, the polymer should be capable of at least uniaxial orientation, and preferably biaxial orientation as well. That is, at normal ambient or elevated temperatures, the polymeric film should stretch more than 50 percent (e.g., at least 100 percent) of its original length without breaking, and significant tensile stress should be exerted by the film during stretching. Stated another way, the film is preferably capable of at least a 1.5:1 orientation along at least one axis. Furthermore, it is essential that, upon release of the stretching force, the stretched film should have and retain some physical change introduced by the stretching, e.g., an at least partially ordered molecular orientation or strain pattern, preferably an orientation along the lines of the stress exerted during elongation. Reference is again made to the polyolefins, e.g., polypropylene, and the polyurethanes, as preferred examples of polymers which have properties which permit uniaxial or biaxial stretch orientation with at least partial retention of stretch-induced characteristics. When oriented at 90°–150°C., even the "elastomeric" urethane-type show some permanent effects from the stretching, e.g., a measurable decrease in film caliper. It has also been found that opacity, softness, or flexibility, and strength are increased by the stretch orientation. These additional benefits can be taken advantage of in a number of ways; for example, the increased opacity can eliminate the need for expensive pigments such as titanium dioxide, though pigments can also be included if desired.

In the present application, stretching is described either as a percent elongation at maximum stretch or as the ratio of stretched length to original length. A stretch ratio of 1.0 would thus be 0 percent elongation

and a stretch ratio of 2 (i.e., 2:1) would be 100 percent elongation.

The uniaxial or biaxial stretch ratio used to stretch orient films of this invention preferably is greater than 1.5 (i.e., 50 percent elongation). The upper limit of uniaxial stretch orientation is determined by the percent elongation-at-break capability of the filled film. Preferred polymers of films of this invention permit a uniaxial stretching or elongation of 300 percent (4:1) or more, particularly at elevated temperatures, with little or no danger of breaking. Polyolefin films may be subject to rupture during biaxial 3 × 3 stretching. Uniaxial orientations of up to 8:1 can be obtained with polypropylene, however. Stretching can be carried out at normal ambient temperatures, but is preferably done at elevated temperatures up to a few degrees below the melting point of the polymer or the temperature at which significant degradation begins to occur, whichever temperature occurs first. Degradation or undue softening of the film can generally be avoided by limiting this elevated temperature range to below about 175°C.

Biaxial stretching, either balanced or unbalanced, is preferred. For polyurethanes, dramatic increases in porosity are achieved by stretching at least 1.5:1 (preferably at least 2:1) in both directions. The increases begin to be less noticeable when the stretch has reached 4 × 4 or even 4 × 2.5. With a stretch of at least 2:1 with polyurethane film (2.5:1 for polypropylene film), the entire film will generally be oriented. Some unoriented areas may occur below these ratios.

As pointed out previously, the stretch-oriented films filled with calcium carbonate particles, or some other suitable non-hygroscopic water-insoluble inorganic metal salt pore-nucleating agent, need not be leached: the pore-nucleating agent remains within the pores of the film, yet the moisture vapor transmission (MVT) and water absorption properties and void volume of the stretch-oriented filled film all appear to be comparable to those of leached films, including stretch-oriented leached films. The "void volume" is determined from the "true density" and "apparent density" of the film. The "true density" is a weighted average of the density of the polymer and the materials incorporated in it, including, of course, the pore-nucleating agent. For example, the "true density" of high density polypropylene filled with CaCO₃ (hexagonal) would be the average of 0.96 g/cc and 2.71 g/cc, respectively, weighted according to the ratio of polypropylene to hexagonal calcium carbonate. A "true density" can also be determined empirically from the weight per unit volume of the filled, unstretched film. The "apparent density" of the porous, stretch-oriented film is its weight per unit of apparent volume (apparent volume includes pore volume). The percent void volume is then given by:

$$\frac{(\text{True Density} - \text{Apparent Density})}{(\text{True Density})} \times 100$$

Void volumes of greater than 5 volume percent and up to about 50 or 60 percent or more can be obtained by the teachings of this invention, even though the resulting porous films still contain 5–60 percent by volume of the relatively dense pore-nucleating agent interspersed throughout the porous polymeric structure. For example, the porous polymeric film could contain about 50 volume percent of pore-nucleating agent within the porous structure and still have a void volume of about 50 percent. The gain in void volume which

would be obtained by leaching out of the filler can readily be sacrificed for the contemplated uses of this invention, thereby eliminating a lengthy leach time and achieving a large saving in plant time, as well as a substantial simplification of manufacturing equipment and procedures.

The liquid-absorptive capacity of the stretch-oriented porous films of this invention can be qualitatively determined by the simple expedient of dripping various liquids onto a film sample. Nonporous films of, for example, polypropylene or filled polypropylene will repel the liquid and the droplets will remain on the surface of the film. The stretch-oriented porous films of this invention, however, are readily permeated by droplets of a wide variety of polar and nonpolar organic liquids and solutions. Water and aqueous solutions also permeate these films with the help of a surfactant. This permeation can proceed all the way through the film sample, indicating an interconnecting pore structure.

Further evidence of an interconnecting pore structure is obtained from photomicrographs and moisture vapor transmission (MVT) studies. A standard MVT test (also called LPV for "leather permeability value" when the sample is a leather-like material) is described in column 7, line 16 et seq. of U.S. Pat. No. 2,723,935 (Rodman), issued Nov. 1955, and is expressed in grams of water per 100 square meters per hour ($\text{g}/100 \text{ m}^2\text{hr}$) for a given temperature relative humidity (R.H.) difference. Other commonly used MVT units are in $\mu\text{gm}/\text{cm}^2 \text{ hr}$. Throughout this application, the R.H. difference for the MVT values has been set at no more than about 100/50 percent but no less than about 100/60 percent, and the temperature was kept at $22 - 24^\circ \text{C}$. ($71.6^\circ - 75^\circ \text{F}$). An MVT of $500 \text{ g/hr}/100 \text{ m}^2$ is considered significant, and an MVT of 8,000 or 9,000 is considered extremely high — higher than typical highly hydrophilic and moisture permeable materials such as leather. Yet MVT values near the upper end of this range, e.g., 3,000 – 7,700, can readily be obtained according to the teachings of this invention without a leaching step. Surprisingly, no gain in MVT can be positively confirmed by leaching the pore-nucleating filler from the stretch-oriented porous film, because the observed "gain" is generally within the limits of the 10 percent experimental error inherent in the aforementioned MVT test. Furthermore, MVT rates of 1,000 – 4,000 are considered good for less demanding uses of moisture permeable films, e.g., in complex laminates such as leather substitutes. The MVT rate for first aid dressings is preferably above 3,000. Another useful index of both porosity and gas permeability can be obtained from Gurley densometer readings, wherein a given volume of air (e.g., 50 cc or 100 cc) traverses a given area of film with a given caliper. The number of seconds should be less than 1,000, preferably less than 400 for 50 cc of air to traverse a square inch (6.45 cm^2) of a porous film with a caliper of about 6 ± 1 mils (150 ± 25 microns). (It should be borne in mind that all film thicknesses specified in this application are subject to caliper control variations of about ± 1 mil, i.e., ± 25 microns.)

The aforementioned photomicrographic studies show cross sections of film with relatively large (e.g., larger than 2 or 3 microns) cavities containing pore-nucleating agents. These cavities appear to be interconnected by sub-micron sized openings or passageways. It is theorized that the sub-micron interconnecting pas-

sages determine the rate of transmission of liquids or gases through the film. The pore size and shape of the stretch-oriented porous films of this invention is determined primarily by two factors: the shape and size of the pore-nucleating particles and the type and amount of stretching. Upon microscopic examination, the pores appear to be larger than the pore-nucleating particles, but these particles do determine the minimum size of the pores. The pores tend to be elongated in shape and have one or more major axes parallel to the axes of stretch orientation. For example, using pore-nucleating orthorhombic or hexagonal particles averaging about 3 microns in their longest dimension, the pores, after stretching of 3:1 (200 percent) or more, average at least 3 or 4 microns in their shortest dimension but more than double, ordinarily more than triple, this amount in their longest dimension. With uniaxial stretching, the pores can be seen to have two short and one long dimension, with biaxial stretching, two long and one short dimension.

To obtain the desired MVT, pore volume, liquid absorptivity, etc., the pore-nucleating agent can be combined with a suitable polymeric matrix in the amount of at least 5 weight per cent of the total weight of film-forming composition, preferable at least 5 volume per cent of the total volume of the film-forming composition. A particularly useful range of pore-nucleating agent content is about 20 to about 75 weight per cent, 40 – 70 wt. percent being typical for the contemplated uses of this invention. The size of the pore-nucleating agent particles can range from colloidal in size to about 25 or 30 microns, for microporous films, and about 25 to about 250 microns, for typical macroporous films. The preferred particle size range for microporous films is about 1 to about 15 microns — for calcium carbonate, this entire range is commercially available. The incorporation of at least 5 wt. percent, preferably at least 20 wt. percent of pore-nucleating agent is normally required to obtain the formation of the high interconnecting void volume of this invention. Stretching alone, even with small amounts (5 wt. percent) of CaCO_3 present, appears to produce primarily discontinuous, unconnected pores. (An interconnecting pore structure can be achieved without a pore-nucleating agent according to the disclosure of U.S. Pat. No. 3,558,764, but this disclosure calls for a multi-step drawing/annealing/cold-drawing/heat-setting procedure which is unnecessary in the present invention.)

The film forming processes used in this invention, e.g., pressing, calendering, or extruding of milled polymer/inorganic salt mixtures, are well known in the art. Heating of the milled mixture is conventionally involved in these film-forming methods. The pore-nucleating particles of the inorganic salt can be added in increments during the milling step. Casting, e.g., of solutions of polymer filled with pore-nucleating particles, is not preferred.

The preferred inorganic fillers used in this invention are non-hygroscopic, light-colored, water insoluble, low density (below 3.0 g/cc), highly pure, easily pulverized (i.e., below about 5 on the Moh's scale) finely divided, high-melting (i.e., above organic polymer degradation or melting ranges) solid inorganic metal salt particles. Calcium carbonate particles, which are preferred, can be in any suitable naturally occurring or man-made form. Naturally occurring forms include the rather pure crystals of calcite (hexagonal calcium car-

bonate) and aragonite (orthorhombic calcium carbonate). The melting point of calcium carbonate (above 800° C.) is far in excess of any temperatures that might be used, even momentarily, to treat an organic polymer; its calcite form is rated at 3 on Moh's Scale of Hardness, barely above gypsum. This degree of softness permits easy and rapid pulverizing. Suitable man-made, highly pure forms of calcium carbonate include precipitated chalk and the like. Very finely divided, pure particles of this carbonate (e.g., 0.05 – 10 microns) are commercially available in large quantities. Calcium carbonate is aptly described as "water insoluble." By "water-insoluble" is meant a solid which cannot be dissolved in deionized water (of pH = 7) to a sufficient extent to form a 0.1 wt. percent aqueous solution at 23° C. Even at 100° C., CaCO₃ will not form even a 0.003 percent aqueous solution in deionized water; about 0.002 percent is its maximum water solubility. The insolubility of calcium carbonate in organic materials such as plasticizers is also a useful property in the context of this invention.

Calcium carbonate is non-hygroscopic in the sense that it does not pick up moisture from the air, and particles of this salt do not have a tendency to "cake" or agglomerate due to absorbed moisture. Commercial grades of sodium chloride, for example, are too hygroscopic to be convenient for use in this invention. The specific gravity of hexagonal calcium carbonate is only slightly above 2.7, and all forms of the salt have a specific gravity of less than 3.

Calcium carbonate is acid sensitive, but is generally non-reactive with organic polymers such as polyolefins and polyurethanes; it is, for all practical purposes, substantially neutral in organic media.

Other inorganic salts with properties similar to calcium carbonate, e.g., the alkaline earth metal carbonates and sulfates of low water solubility such as magnesium carbonate, calcium sulfate, and barium sulfate, can be substituted for calcium carbonate in this invention. Generally, however, these other salts lack one or more advantage of calcium carbonate. Barium sulfate is water insoluble, soft (2.5 – 3.5 on Moh's scale), very high melting, and generally white or light colored in finely divided form, but its specific gravity of almost 4.5 detracts from the prospect of making light weight films which contain high loadings of unleached filler.

Calcium sulfate is low in hardness, low in density, light in color, and very high melting, but is more water soluble than calcium carbonate. Being capable of acidic behavior, this salt is not neutral and may react with some organic polymers at elevated temperatures. Magnesium carbonate is more neutral and water insoluble, but is slightly harder, slightly denser, and subject to decomposition at relatively low temperatures, e.g., 350° – 400° C. Generally the organic polymers used in this invention are not subjected to any heat treatments involving temperatures above 200° C.; however, many organic polymers will withstand very brief heat treatments at temperatures near the decomposition temperature of magnesium carbonate. It is useful to have the wide safety factor provided by the extremely high melting points (above 400° C.) of the preferred inorganic fillers of this invention. It is within the scope of this invention to use colored forms of the pore-nucleating agent, or to add color to it. Calcite, for example, occurs naturally in a wide variety of colors. As has been pointed out previously, the pore-nucleating agent can

do double duty as pore-forming and pigmentation agent. The pore-nucleating agents, after stretching, are located within the walls of the pores or otherwise associated with the porous film structure, and can impart both color and opacity to the stretch-oriented, microporous films of this invention.

Stretch-oriented, macroporous or microporous polymeric films containing the pore-nucleating agent can be made according to this invention within a wide range of film thickness or caliper. For the uses contemplated for this invention, a thickness of less than about 2 mm. (80 mils) is generally preferred. Films having a thickness in the range of about 0.1 to about 1 mm (about 0.5 – 40 mils) are particularly useful. As pointed out previously, a measurable decrease in caliper or thickness normally occurs after stretch-orientation. Even for a uniaxial orientation, this decrease can be as much as about one-third of the unoriented film thickness. For biaxial orientation and extremely large uniaxial orientations, the decrease in thickness can be still greater.

The polyolefin most preferred for use in the present invention is polypropylene of either the low density (0.90 g/cc) or high density (0.96 g/cc) grades. Polyurethane polymers used in the present invention are preferably derived from aliphatic or aromatic di- or triisocyanates and polyesters or poly(oxyalkylene) diols or triols of 200 – 10,000 (preferably 400 – 6,000) molecular weight. It is permissible to use polyesters or polyethers terminated with other than OH radicals, e.g., mercaptans, primary or secondary amines, carboxyls, or other active-hydrogen-bearing substituents. Chain extenders and/or crosslinkers terminated with such active hydrogen-bearing substituents are usually included in the polymer preparation. It is surprising that elastomeric polyurethanes behave analogously to the polypropylene with respect to increasing MVT by stretch orientation.

The stretch-oriented porous films of this invention (particularly the microporous films) can be adapted for use in a variety of applications, as films per se, preferably, as printed, coated, or laminated articles. That is, these films can be combined with coatings, additional film-like or fibrous laminae, etc. Among the applications contemplated for this invention are filters, breathable bandages, and other vapor permeable first aid dressings, surgical drapes and similar medical products, conformable and printable backings for coated and laminated articles, typewriter and other inking ribbons and sheets or pads, breathable garments, or clothing materials of footwear such as leather substitutes or rainwear, battery separators (particularly in alkaline batteries), breathable shoe inserts or insole material, flexible gas-permeable containers (e.g., sterilizable packages for surgical instruments; see U.S. Pat. No. 3,332,549, issued July 25, 1967) and the like.

Examples of known coating and laminating techniques can be found in the prior art already cited and in, for example, U.S. Pat. No. 2,826,509. The stretch-oriented porous films can be made with varying degrees of rubberiness, flexibility, rigidity, porosity, liquid-absorptivity, moisture vapor transmission, and ion-transfer characteristics, depending on the use contemplated. Fillers, in addition to the pore-nucleating agents, can be added to modify these various properties. Wetting agents or surfactants can be added to the stretch-oriented porous films to alter or improve their

absorptivity of polar liquids, including water. For example, a stretch-oriented microporous polypropylene film of this invention will not normally permit water to pass all the way through the thickness of the film, but suitable wetting agents will readily promote liquid water penetration.

A particularly useful application of the stretch-oriented microporous films of this invention is to provide a polymeric film with many of the characteristics of writing paper. For example, films of this invention with a high void content are flexible, conformable, tearable, fine-textured, and opaque white in color, and thin and sheet-like, much like paper stock. Furthermore, the high void content and permeability of the film provides good ink and dye anchorage. Such films can readily be written on either surface with an oleaginous printing ink, a fountain pen ink, or the like.

In summary, the contemplated composites or fabricated products containing stretch-oriented microporous films of this invention are coated, laminated, liquid (e.g., ink) -impregnated articles, or articles having indicia printed on at least one surface of the stretch-oriented porous film.

The following non-limiting examples illustrate the invention.

EXAMPLE 1

Four hundred grams of polypropylene resin ("Profax 6723" — Hercules, Inc.) was banded on a two-roll rubber mill heated at 380°–390° F. (193–199° C.). After banding (2 minutes), 900 g. CaCO₃ was added to the mill. The CaCO₃ was "Non-Fer-Al" Grade obtained from Diamond Chemical Company. This was a highly pure grade (99.3% CaCO₃) with an average particle size of 3 microns diameter and a range of 1–10 microns diameter. The major impurity was CaSO₄ (0.5%). The pH was 9.4. About 15 minutes was required for complete dispersion of the CaCO₃ in the polypropylene. Next, the mill stock was knifed off the mill and cooled. A 15 g. sample was next pressed in a Pasadena Hydraulic press between sheets of polytetrafluoroethylene film. The press was maintained at 425° F. (218° C.). A force of 30,000 lbs. (13,600 Kg) was applied. The film sample was removed after pressing about 30 seconds. Next, a strip of film 2 inches wide and 6 inches long (5.1 × 15 cm) was placed in a Thelco forced air lab oven maintained at 110° C. Film caliper was 9 ± 1 mils (0.230 ± 0.025 mm). After heating for 3 minutes, the oven door was opened and the film strip was stretched uniaxially by hand in the oven until it was uniformly opaque white. Final stretch ratio was 4 to 1. A sample of unstretched film had a measured density of 1.59 g/cc. The density of the stretched film was 0.87 g/cc. The percent voids in the stretched film then was 45 percent by volume. The moisture vapor transmission (MVT) rate was 4,900 g/hr/100 sq. meters measured at a relative humidity difference of 100 to 50 percent and a temperature of 73° F. (23° C.). The stretched film was immediately permeated through by drops of 1,1,2-trichloro-1,2,2-trifluoroethane ("Freon" 113), chloroform, toluene, methyl ethyl ketone, a commercial oil based red rubber stamp pad ink, and opaque black pigmented Flowmaster pen ink. Film bending modulus was greatly reduced by the stretching.

The microporous film produced by this Example was found to be particularly suitable for use in the first aid dressing of FIG. 1 and the sterilizable bag of FIG. 4.

EXAMPLE 2

Part A: Stretch-oriented Polyurethane Films

The polyurethane used in this Example was "Estane" 5707-F-1 polyesterurethane (trademark of B. F. Goodrich Chemical Company) derived from 1.00 mole poly (1,4-butylene adipate) glycol, 1.85 moles 1,4-butane diol, and 2.85 moles diphenylmethane-p,p'-diisocyanate. Solid "Estane" polyurethane pellets were milled with enough calcium carbonate to provide a mixture comprising 61 wt. percent calcium carbonate. The polyurethane/CaCO₃ mixture was then extruded to form a film of 11 ± 1 mils (0.280 ± 0.025 mm) caliper. Eight samples (Sample A — Sample H) were obtained in this manner. The extruded (but otherwise unstretched or unoriented) 11 mil film had an MVT rate of 49.5 microgram/cm²hr. A Gurley Densometer reading was then taken (see, for example, ASTM test D726); which involves forcing a given quantity of air through a given cross-sectional area of a film and measuring the time (in seconds) required to force the air through. The Gurley reading varies with the caliper of the film. For the non-stretch oriented 11 mil film, no Gurley reading could be obtained, indicating that the film was substantially impermeable to air under the test conditions. A 2:1 uniaxial stretch orientation (Sample A) reduced the caliper to 10 ± 1 mils (0.250 ± 0.025 mm) and increased the MVT rate to 3,260 microgram/cm²hr, but the Gurley reading still indicated a substantially air-impermeable film. Significantly increased porosity measurements were observed with 3:1 uniaxial stretching and biaxial (up to 3 × 4) stretching, although the Gurley and MVT data did not correlate perfectly. The results are tabulated in Table I. All MVT rate measurements were taken at 72° F. (22° C.) and a 100/57 percent relative humidity (RH) differential. Film calipers in Table I were measured after orientation in mils. Caliper measurements are accurate to ± 1 mil (± 0.025 mm) and MVT rate measurements are subject to an experimental error which can be as high as 5 percent. Gurley porosity readings were taken using 50 cc of air and a one square inch (6.45 cm²) area of film.

TABLE I

Polyurethane/CaCO ₃ Film Samples Stretch-Orientation vs. Porosity				
Sample	Orientation	Film caliper in mils (mm)	MVT (μg/cm ² hr)	Gurley Porosity (sec/50 cc-in ²)
Un-stretched	1 × 1	11 (0.28)	49.5	not permeated
A	2 × 1	10 (0.25)	3260	not permeated
B	3 × 1	6 (0.15)	5172	75
C	3 × 1.5	6 (0.15)	6380	90.3
D	3 × 2	6 (0.15)	6670	78.7
E	2.5 × 2.5	6 (0.15)	7090	50.1
F	3 × 3	6 (0.15)	7500	29.9
G	2.5 × 4	6 (0.15)	7640	36.5
H	3 × 4	6 (0.15)	5172	22.9

Part B: Effect of Leaching

For comparison, the "unstretched" (1×1 orientation) 11 mil polyurethane/ CaCO_3 film of Example 2(A) was leached to approximately 40 percent of its original weight with hydrochloric acid, and the MVT of the leached film was measured under previously described conditions. The MVT rate was found to be only 425 microgram/ cm^2hr , a relatively insignificant value as compared to the MVT's of any of Samples A - H.

A second set of samples were prepared by dissolving 100 parts by weight of the "Estane" 5707-F1 (polyesterurethane—see Example 2(A) and dispensing 180 parts of sodium chloride in the solution. Films were cast from the solution and the solvent was removed. The sodium chloride was leached from the cast and dried films without any stretch orientation prior to leaching. MVT rates for three different calipers of leached, unoriented film are set forth in Table II.

TABLE II

Polyurethane/ NaCl Films (Leached, Unoriented)	
Caliper in mils (mm)	MVT ($\mu\text{g}/\text{cm}^2\text{hr}$)
15 (0.38)	8435
10 (0.25)	9000
6 (0.15)	9020

These MVT data reflect the lower density, hence higher volume of sodium chloride filler prior to leachings and higher void volumes after leaching. Otherwise the data show little, if any, improvement over Samples A - H.

EXAMPLE 3

In this Example, porous polypropylene films were made from "Profax 6723" (trademark of Hercules, Inc.) and calcium carbonate, as in Example 1, except that film samples were extruded. Both uniaxial orientation ($2:1$, $3:1$, and $4:1$ in the machine direction) and biaxial orientation (2×2 and 3×3 , machine direction \times cross direction) were used to obtain porosity, and the effect of varying the amount of calcium carbonate filler from 50 - 200 parts by weight per 100 parts by weight of polypropylene (phr) was also investigated by making samples from four lots of material:

Lot	wt. % CaCO_3	phr	Polypropylene (wt. %)
1	33.3	50	66.6
2	50	100	50
3	60	150	40
4	66.6	200	33.3

Film calipers were generally 6 or 7 ± 1 mil.

The Gurley Densometer readings are tabulated in Table III.

TABLE III

Porosity of Non-leached, Stretch Oriented, CaCO_3 -Loaded Films: Orientation and Amount of Filler vs. Gurley Porosity				
Amt. of Filler (phr)	Orientation (machine dir. \times cross dir.)	Gurley Densometer Readings in seconds/volume/sq. inch (6.45cm^2)		
		sec/10cc	sec/50cc	sec/100cc
50	2×1	1000	1000	1000
100	2×1	1000	1000	1000
150	2×1	100	397	878
200	2×1	37	136	282
50	3×1	1000	1000	1000
100	3×1	497	1000	1000
150	3×1	29	172	343
200	3×1	14	63	150
50	4×1	1000	1000	1000
100	4×1	239	1000	1000
150	4×1	25	104	205
200	4×1	9	46	99
50	2×2	1000	1000	1000
100	2×2	156	721	1000
150	2×2	11	65	165
200	2×2	6	30	66
50	3×3	(broke during orientation)		
100	3×3	32	121	252
150	3×3	1	6	16
200	3×3	1	5	11

EXAMPLE 4

The effect of leaching porous polypropylene films made from Lot 4 (200 phr calcium carbonate) by making additional comparative samples was investigated. The comparative samples contained a leachable filler, in this case 225 parts by weight of sodium chloride for each 100 parts by weight of "Profax" 6723 polypropylene. The sodium chloride-containing comparative samples were leached free of the filler with water and then measured for MVT rate, but the Lot 4 samples were measured for MVT rate without any leaching step. All samples were stretch oriented at 4×1 or 3×2 . The comparison is set forth in Table IV.

TABLE IV

Effect of Leaching On Stretch-Oriented Films			
Filler (phr)	Leached	Orientation (mach. dir. \times cross dir.)	MVT ($\mu\text{g}/\text{cm}^2\text{hr}$)
225 NaCl	Yes	4×1	4675
225 NaCl	Yes	3×2	4925
200 CaCO_3	No	4×1	4475
200 CaCO_3	No	3×2	4950

The differences in MVT rate between leached and unleached films were not significant in view of the experimental error of the MVT determination.

In the preceding Examples, the MVT rate was measured according to the method described in Elton, U.S. Pat. 3,640,829, issued Feb. 8, 1972. Sufficient control of ambient humidity was maintained to keep the experimental error in this test to within 5 percent, except for Example 1, where the error was believed larger, though within 10 percent.

What is claimed is:

1. A stretch-oriented, elastomeric, porous polyurethane film less than 80 mils in thickness having a void volume of about 5 - 60 volume percent, said void volume being in the form of an interconnecting network of voids, said voids averaging about 3 - 250 microns in

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their longest dimension, said polyurethane film having been stretch-oriented at a stretch ratio of at least 1.5:1 in at least one direction, thereby being enlarged in area to at least 1.5 times as large as the original area and thereby being decreased in thickness, said polyurethane film containing 5 to 60 percent by volume of an inorganic water insoluble pore nucleating agent distributed throughout said interconnecting network of voids and being smaller in average size than the said average size of said voids, said polyurethane film having a moisture vapor transmission value of at least 500 microgram/cm²hr for a relative humidity difference on opposite sides of said polyurethane film of no less than

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100/60 percent.

2. A polyurethane film according to claim 1 wherein said film is coated with a pressure-sensitive adhesive.

3. A film according to claim 2 wound upon itself to form a roll comprising a plurality of convolutions.

4. A film according to claim 1 laminated to a nonadherent, moisture-transmissive burn covering material.

5. A film according to claim 4 wound upon itself to form a roll comprising a plurality of convolutions.

6. A first aid dressing comprising a film according to claim 1 laminated to an absorbent pad.

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